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Liners of Natural Porous Materials to Minimize Pollutant Migration

Arizona Agricultural Experiment Station
Tucson

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

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LINERS OF NATURAL POROUS MATERIALS TO MINIMIZE POLLUTANT MIGRATION

by

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Grant No. R 803988

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This is a report of the relative effectiveness of natural low-cost liners of crushed limestone, clayey soil, hydrous oxides of iron, and crushed pecan hulls for minimizing the migration of Be, Cd, Cr, Fe, Ni, Zn, and total organic carbon constituents of municipal solid waste landfill leachates. Several leachate variables such as aqueous dilution, aeration, pH, and flux were also studied for their effect on movement of metals through 11 representative U.S. soils. The research was conducted on a laboratory scale using soil columns as a first step in screening for potential liners and manipulation practices. Limestone and hydrous iron oxide were found to be potentially useful as porous liners for retention of metallic leachate constituents. The amounts of these materials in natural soils were also found to be useful predictors of contaminant removal.

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*Hazardous Materials	Copper	Pollutant Migration	13B
*Transport Properties	Chromium	Groundwater Pollution	
*Soil Chemistry	Iron	Municipal Solid Waste	
Attenuation	Lead (Metal)	Leachate	
Contaminants	Mercury (Metal)	Landfill Liners	
Arsenic	Selenium		
Beryllium	Zinc		
Cadmium	Industrial Wastes		

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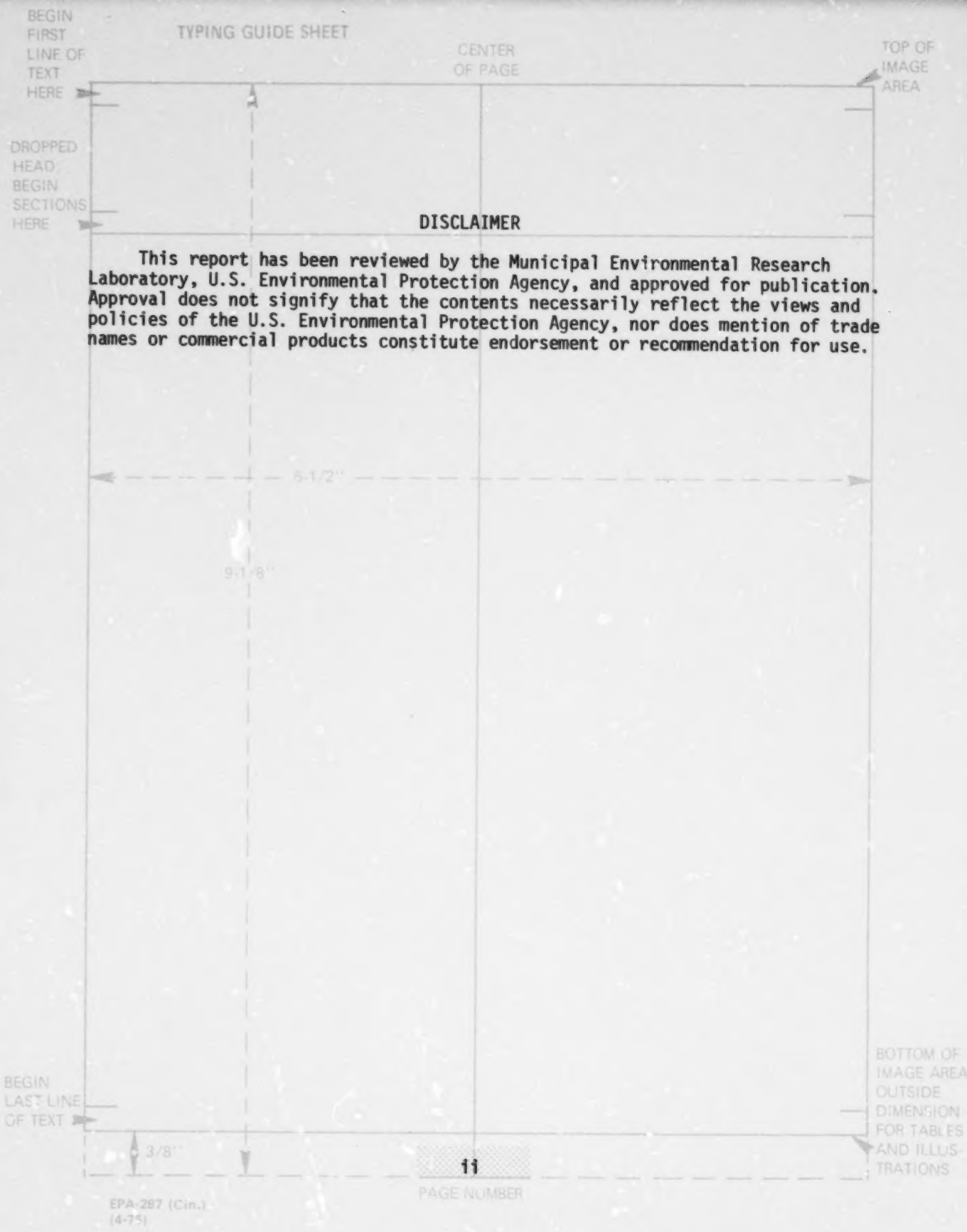

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FOREWORD

The Environmental Protection Agency was created because of increasing concern by the public and government about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development--that necessary first step in solving a problem--involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to preserve and treat public drinking water supplies, to minimize the adverse economic, social, health, and aesthetic effects of pollution and to prevent, treat, and manage waste water and solid and hazardous waste pollutant discharges from municipal and community sources. This publication is one of the products of that research; it is a vital communications link between the researcher and the community.

Results are reported from laboratory study of porous liners for landfills that allow leachate to pass through while retaining pollutants. Materials studied include not only soil but also agricultural limestone, iron oxide, and nuthulls. The results are applicable to the design of liners for landfills and other disposal facilities.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

When landfills are not completely impermeable then underlying groundwater may be contaminated by leachate constituents if these are not adequately retained by soils between the landfill and groundwater. Research on industrial waste disposal has centered on use of manufactured products such as plastics and cementing roadbed materials such as asphalt and concrete to alleviate this problem by completely preventing liquid movement out of the landfill. Little attention has been given to use of natural low-cost materials as barriers for minimizing pollution migration by retaining contaminants from liquids as they pass out of landfills.

This is a report of the relative effectiveness of natural low-cost liners of (a) crushed limestone, (b) clayey soil, (c) hydrous oxides of iron, and (d) crushed pecan hulls for minimizing the migration of beryllium, cadmium, chromium, iron, nickel, zinc, and total organic carbon constituents of municipal solid waste landfill leachates. Several leachte variables such as aqueous dilution, aeration, pH, and flux also were studied for their effect on movement of metals through 11 representative U.S. soils. The research was conducted on a laboratory scale using soil columns as a first step in screening for potential liners and leachate manipulation practices.

Limestone and hydrous iron oxide were found to be potentially useful as porous liners for retention of metallic leachate constituents. The amounts of these materials in natural soils were also found to be useful predictors of contaminant removal from leachate.

This report was submitted in fulfillment of Grant No. R 803988 by The University of Arizona under the partial sponsorship of the U.S. Environmental Protection Agency. The report covers the period of October 1975 through September 1977 and the work was completed as of October 1977.

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TOP OF IMAGE AREA
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CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables viii
Abbreviations and Symbols x
Acknowledgment xii

1. Introduction 1
2. Conclusions 4
3. Recommendations 6
4. Materials and Methods 8
5. Results and Discussion 24

Leachate variables affecting metal movement from landfills 24
Effect of aeration with O_2 and CO_2 25
Effect of aqueous dilution and pH 26
Effect of organic carbon (TOC) and salts 34
Effect of specific ion concentration 34

Solution flux affecting metal movement from landfills 38
Flux and leachate variables 38
Flux and soil variabiles 42
Flux and metal variables 42
Flux and metal concentration 50

Crushed limestone liners 50
Cations - Be, Cd, Fe, Ni, and Zn 50
Anions - As, CrVI, Se, and V 57
Organic carbon 57
Limestone utilization 62

Natural soil liners and salt modification liners 65

Specialty liners 65
Hydrous-oxides of iron 65
Nutshells and similar organics 66

References 69

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EPA-287 (Cin.)
(4-76)

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TOP OF IMAGE AREA
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FIGURES

Number		Page
1	Schematic of migration rates versus soil-leachate-element system.	2
2	Ratio of effluent concentration to influent concentration (C/Co; where C/Co = 1 is breakthrough) plotted against time (or pore volume displacement).	21
3	Trajectaries of different relative concentrations. (Plot of Z = Z(t), where Z = (Zt) satisfied $C(t,z(t)) = C_1$, i = 1, 2, 3, 4, 5.	22
4	Effect of aeration on the pH of municipal solid waste Leachate I.	27
5	Effect of aqueous dilution on Cd concentrations in soil column effluents moving through Ava sicl at a flux of 8 cm/day.	29
6	Influence of aqueous dilution and pH on the solubility of CrVI enriched into Leachate I at 100 ppm after stabilization of 48 hrs.	33
7	Effect of total organic carbon constituents, salt, and iron on the migration rate of Fe from Leachate II through Kalkaska sand.	35
8	Effect of total organic carbon constituents, salt, and iron on the migration rate of Cd from Leachate II through Ava silty clay loam.	36
9	Migration rates of Cr in MSW landfill Leachate I in Kalkaska s and Fanno c as related to three solution flow rates (flux).	39
10	Migration rates of Cd and Cr in MSW landfill Leachate I through Fanno c as related to three flow rates	40
11	Migration rate of Cd in MSW landfill Leachate II in six soils as related to two solution flow rates (flux)	44

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PAGE NUMBER
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3/8"
9-1/8"
PAGE NUMBER
EPA-287 (Cin.) (4-76)

12 Influence of widely varying fluxes of MSW landfill Leachate II on Cd retention by Ava si c l. +Flux (flow velocity is expressed as discharge (cm^3) per unit area (cm^2) per day (cm/day will relate as measured rainfall) 45

13 Nickel attenuation in six soils as influenced by different flow rates (flux) of MSW landfill Leachate II 46

14 Zinc attenuation in six soils as influenced by different flow rates (flux) of MSW landfill Leachate II. 47

15 Beryllium attenuation in three soils as influenced by different flow rates (flux) of MSW landfill Leachate II 48

16 Effect of crushed limestone layered (2 cm) over six soils on the retention of Fe from MSW landfill Leachate II. 52

17 Relative migration rates of CrVI and CrIII enriched as CrVI into landfill Leachate II through 2 cm layer of crushed limestone over 10 cm coarse quartz sand 58

18 Effect of the hydrous oxides of iron precipitated on Anthony sl and Wagram s on attenuation of CrVI and Ni of MSW Leachate I 67

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE

TABLES

Number		Page
1.	General Characteristics of the soils	9
2.	Some Chemical Characteristics of Water-Saturated Paste Extracts of Soils Studied . .	10
3.	Total Analysis of Soils for Trace Metals and Free Iron Oxides . .	11
4.	Composition of Solid Waste used to Generate Leachate	12
5.	Some Chemical Characteristics of Leachate I (Concrete Generator) .	14
6.	Some Chemical Characteristics of Leachate II (Steel Generator) . .	16
7.	Particle Size Distribution of Agricultural Limestone from Three Kentucky Sources . .	18
8.	Effect of Exposure to Air, CO_2, and Acidification on the Fe and Mn Solubility of Solid Waste Leachate I . .	25
9.	Effect of Aeration with CO_2 and Air on the Solubility of 12 Trace Elements Enriched Singly to Municipal Solid Waste Leachate II .	28
10.	Effects of pH, Contact Time, and Aqueous Dilution on Concentration of Cr, Fe, TOC, and EC in Leachate II . .	31
11.	Effect of Dilution of MSW Leachate II with Water on the Solubility of Cr and Fe, and TOC, pH, and EC	32
12.	Effects of Different Concentrations of Organic Carbon and Soluble Inorganic Salt in MSW Leachate II on the Ni Retained by Six Soils	37
13.	Effects of Different Concentrations of Organic Carbon and Soluble Inorganic Salt in MSW Leachate II on Zn Retained by Seven Soils	37
14.	Comparison of Fe and Al Attenuation at Two Solution Flow Rates Through Nicholson sic . .	41
15.	Influence of Flux on the Retention of Cd from MSW Landfill Leachate I by Three Soils	42

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BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.) (4-78)

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DROPPED HEAD: BEGIN SECTIONS HERE

TABLES (continued)

Number		Page
16.	Effect of Flux on the Retention of Selected Metals in MSW Landfill Leachate II passed through nine soils	49
17.	Cadmium Attenuation as Influenced by Flux and Metal Concentration in MSW Landfill Leachate II passed through Ava Silty Clay Loam	51
18.	Relative Effect of Crushed Limestone Liner Placed over Soil on the Rate of Migration of Cation-Forming Metals in MSW Landfill Leachate I	53
19.	Retention of Fe from Natural Municipal Landfill Leachate II passed through 11 Soils as Related to Unit Weight and Surface Area	55
20.	Effect of Crushed Limestone Liner and Leaching with Deionized Water on the Retention of Soluble Iron from Natural Landfill Leachate passed through 11 Soils	56
21.	Relative Effect of Crushed Limestone Liner Placed over Soil on the Rate of Migration of Anion-Forming Metals in MSW Landfill Leachate I	59
22.	Effect of Limestone Alone and Limestone Layered over Soils on The Attenuation of Cr in MSW Landfill Leachate II	60
23.	Effect of Crushed Limestone Liner on the Retention of Total Organic Carbon from Natural MSW Landfill Leachate II Passed through Soil and Sand	61
24.	Ability of MSW Landfill Leachate II to Solubilize Limestone Placed over Soil and Quartz Sand Alone	63
25.	Limestone Layered at Four Thicknesses over Sand or Soil Solubilized by MSW Leachates I, II, and III after 20 Pore Volume Displacements	64
26.	Effect of Ground Iron Rust Barrier on Attenuation of CrVI and Ni in MSW Leachate I passed through Anthony sl and Wagram s	68

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PAGE NUMBER
EPA-287 (C.R.)
(4-76)

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

A horizons	-- soil surface or uppermost layer of soil accumulating organic matter
BD	-- bulk density
BOD	-- biological oxygen demand
c	-- clay, < 2μ particles
C/C_o	-- concentration of input solution (influent)/concentration of output solution (effluent)
CEC	-- cation-exchange capacity in soil
cl	-- clay loam
cm	-- centimeter ≃ 0.394 inches
C_{max}	-- maximum concentration of a psecific element
COD	-- chemical oxygen demand
EC	-- electrical conductivity of a solution expressed as mhos, mmhos or μmhos/cm
EDTA	-- ethylene diamine tetraacetic acid
Eh	-- reduction/oxidation factor
g	-- gram
g/cc	-- gram per cubic centimeter
hr	-- hour
ION	-- concentration of soluble ions
kg	-- kilogram
km	-- kilometer ≃ 0.621 mile
l	-- liter ≃ 0.946 quart
lb	-- pound, 454 grams
ls	-- loamy sand
m	-- one meter ≃ 39.4 inches
meq	-- milliequivalence
meq/100 g	-- milliequivalence per 100 grams
mg	-- milligram
mhos	-- reciprocal of ohms
ml	-- milliliter
mm	-- millimeter
mmhos	-- millimhos
pH	-- hydrogen ion activity (0-12)(acid--less than 7.0; alkaline--greater than 7.0)
ppb	-- parts per billion
ppm	-- parts per million
ps	-- pore space
pv	-- pore volume
red/ox or redox	-- reduction/oxidation ratio

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PAGE NUMBER
A-287 (Cin.) 14-76

s	-- sand
si	-- silt
sic	-- silty clay
sicl	-- silty clay loam
sil	-- silty loam
sl	-- sandy loam
TDS	-- total dissolved solids
TOC	-- total organic carbon

SYMBOLS

$AlCl_3$	-- aluminum chloride
As	-- arsenic
Be	-- beryllium
C	-- carbon
Cd	-- cadmium
Cl	-- chloride
Co	-- cobalt
CO_2	-- carbon dioxide
CO_2-tension	-- carbon dioxide partial pressure
CO_3	-- carbonate
Cr	-- chromium
CrIII	-- trivalent chromium (acts as cation)
CrVI	-- hexavalent chromium
Cu	-- copper
Fe	-- iron
$FeCl_2$	-- ferrous chloride
Fe^{++}(FeII)	-- ferrous
Fe^{++}(FeIII)	-- ferric
Fe_2O_3	-- iron oxide (ferric)
H^+	-- hydrogen ion
HCO_3	-- bicarbonate
Hg	-- mercury
m^2	-- square meter
Mg	-- magnesium
Mn	-- manganese
Ni	-- nickel
P	-- phosphorus
Pb	-- lead
PO_4	-- phosphate
Se	-- selenium
SO_4	-- sulfate
V	-- vanadium
Zn	-- zinc
µ	-- micron, micro-
µg	-- microgram (10^{-6} gram)
µg/l	-- micrograms per liter
µmhos	-- micromhos
µmhos/cm	-- micromhos per centimeter
~	-- approximately
≈	-- approximately equal to

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Contributing investigators include B.A. Alesii, A. Amoozegar, J. Artiola, M. Boyle, G.E. Carter, and E.E. Niebla, all of the Department of Soils, Water and Engineering, The University of Arizona, Tucson.

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SECTION 1

INTRODUCTION

There are three main components of the waste disposal environment:

1. Porous medium through which the constituent is being transported (soil),
2. Solution carrying the pollution constituent (leachate),
3. Constituent itself (soluble element involved such as Be, Cd, Cr, Cu, Fe, Ni, Zn, and TOC).

The characteristics of each component markedly influence rate of movement of the pollution constituent through soil used as pollution barriers and/or landfill liners. The interaction of these 3 components of the disposal site may be visualized graphically as a migration rate surface above the equilateral triangle shown in Figure 1. The peaks represent the most rapid movement and the valleys, the least. Since this diagram originates from random data, it cannot be used in its present form to plan real field events. It is presented wholly for the purpose of demonstrating the interaction concept. Further experimental data must be obtained to make such a concept functional.

Lime, clay, and hydrous oxides of iron (probably Mn and Al, also) stand out as soil constituents that influence attenuation of selected metals according to recently accumulated data, Fuller (1978), Korte et al. (1976). These properties assume the position of controllable variables for metal attenuation because soil disposal excavations, typified by landfill sites, may be lined easily to various thicknesses of these materials and packed to densities to achieve a favorable solution flux. In this way, leachates and other waste waters from disposals must pass through a control barrier before entering the natural soil and geological material. Minimizing the threat to food producing soil and groundwater pollution by implementation of low-cost barriers or landfill liners is an attractive concept, particularly in view of data generated, Korte et al. (1975; 1976b) on trace element movement in soil. Data are presented showing it is possible to predict the relative migration rates of certain metals on the basis of soil properties. More recently, data from this same laboratory, O'Donnel et al. (1977) and Fuller et al. (1979a), was developed for use in quantitatively predicting the migration rate of Cd, Ni, and Zn on the basis of known soil and municipal solid waste leachate properties.

OBJECTIVES

The general objective of the research described in this report was to evaluate some low cost landfill disposal site liners (such as crushed lime-

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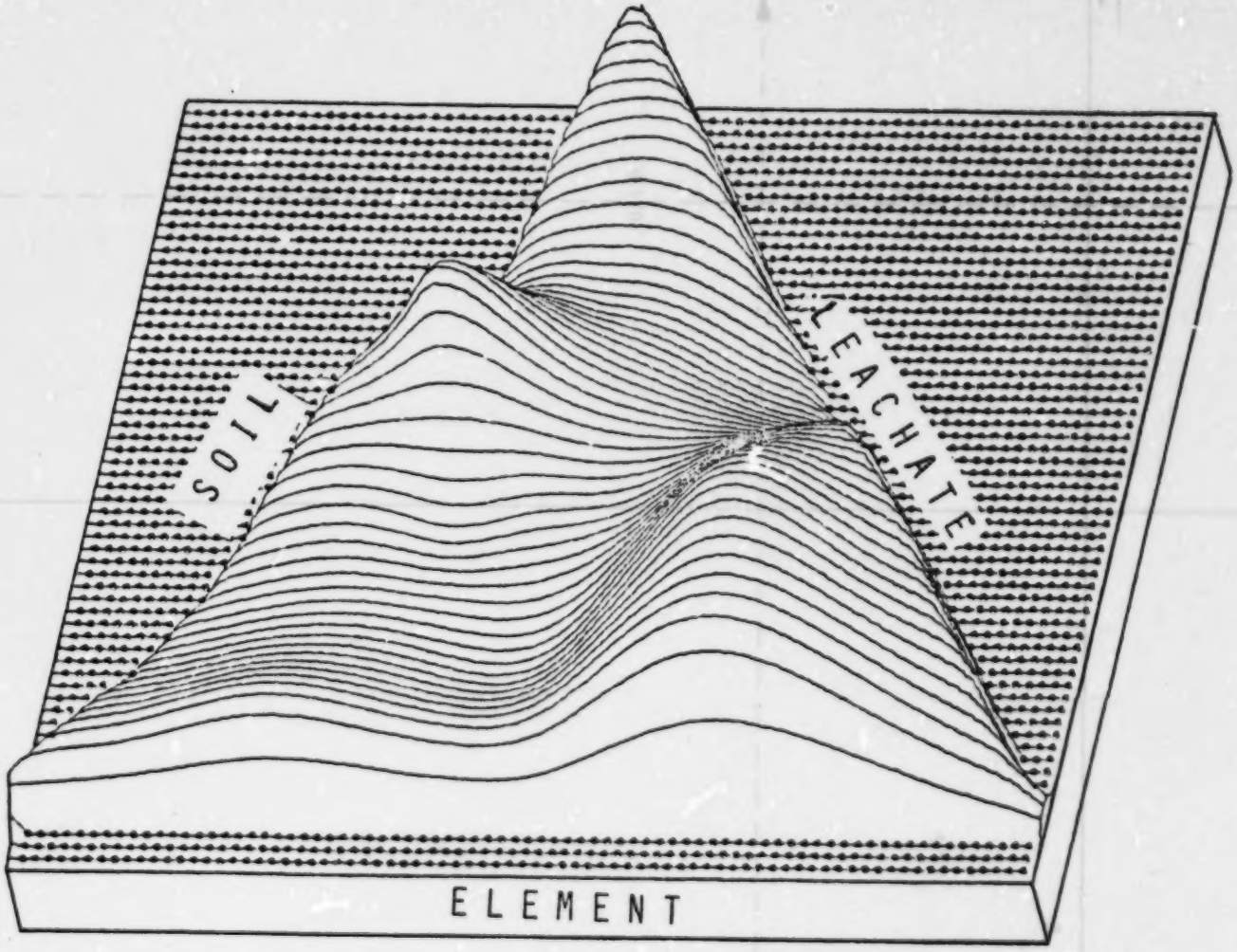

Fig. 1.SCHEMATIC OF MIGRATION RATES VS. SOIL-LEACHATE-ELEMENT SYSTEM

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stone, hydrous oxides of iron, clay soil) to minimize migration of pollutants through soils. The specific objectives researched may be categorized as follows:

1. Identify further those parameters in soil, municipal solid waste landfill leachate, and selected metals that influence movement of polluting contaminants through soils.

2. Evaluate crushed limestone as a liner to limit metal movement from landfills.

3. Evaluate hydrous oxides of iron, natural clays, and pecan hulls as liners to limit metal and organic constituent movement from landfills.

4. Study control of leachate flux to limit migration of metals and organic carbon constituents through soils.

5. Interpret the basic principles developed in this research in terms of practical application for disposal site location and management to minimize pollutant movement from landfills.

The elements in wastes that were considered include: arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), iron (Fe), nickel (Ni), selinium (Se), vanadium (V), and zinc (Zn) as well as total organic carbon (TOC).

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SECTION 2

CONCLUSIONS

1. The composition of municipal solid waste (MSW) leachate (particularly with reference to TOC content, total ion concentration, and pH) exercises a profound influence on retention of the metals As, Be, Cd, Cr, Fe, Ni, Se, V, Zn, and the more common elements Ca, K, Na, and Mg.

2. An abundance of electron donors (TOC and Fe^{+2}) in leachates combined with acidity reduction either naturally by aging or by insertion of a limestone barrier encourage chromium retention by soil through the mechanism of valency change of CrVI to CrIII. CrIII, a cation, is less mobile than CrVI, an anionic form.

3. When placed in layers over soil, crushed agricultural limestone:

    a. Significantly slows the rate of movement of As, Be, Cd, CrIII, Fe, Ni, Se, V, and Zn through soil.

    b. Affects metal retention in the following order of decreasing values:

        CrIII>Se>As>V>Be>Zn>Ni>Fe>Cd>CrVI>TOC.

    c. Exhibits metal retention effects several times greater than when limestone or soil alone is used (a synergic effect).

    d. Is poorly effective for TOC attenuation in MSW leachate.

    Thick layers of crushed limestone (5, 10, 15 cm) provide a more effective barrier than thin layers (2 cm) for MSW leachate metal migration through soils.

4. Leachate flux through soil columns has a significant influence on attenuation of certain metal ions in MSW leachates when flow rates are between 2 and 12 cm/day. The effect of other leachate variables such as pH or concentration of TOC or inorganic salts so overshadow the flux effect that it is difficult to separate flux effects on metal attenuation from the effects of other variables.

5. Hydrous oxides of iron, either formed by spraying soils or sands with ferrous sulfate or iron rust placed as a layer of 1 mm over soil, delay migration of soluble Fe and Cd.

6. It has been found in other studies that natural clay soils (20% <2μ clay), compacted to known homogeneous densities with sufficient sodium salts (Na_2CO_3, NaCl) to provide greater than 20% of cation-exchange-capacity saturation, may be so manipulated as to prevent downward movement of MSW leachate, solution, and all pollutants nearly completely.

7. The data reported here (except item 6) are the result of laboratory studies only and are intended as a first step in screening potential liners. They do not form a sufficient basis for exact liner design. The complex nature of the interactions of soil, leachate, and pollutants require field testing before final applications can be recommended.

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SECTION 3

RECOMMENDATIONS

1. Because soils are highly stratified under natural conditions, soils underlying the disposal site must be made homogeneous as practical by mixing and compacting to assure minimum migration of pollutants from solid waste landfills.

2. The use of crushed limestone should be considered for minimizing movement of potentially hazardous pollutants such as As, Be, Cd, Cr, Fe, Ni, Se, V, and Zn.

3. Layering of limestone over soil as a barrier between MSW landfill leachates and geological materials underlying the landfill is recommended over mixing limestone and soil together or mixing limestone with the solid waste.

4. A layer of crushed limestone about 15 cm (6 in.) thick is suggested as minimum at most disposal sites, but specific wastes and soils should be tested before a precise thickness is finally selected for a given site.

5. The particle sizes of crushed agricultural limestone that are generally available commercially appear to be suitable for use but field verification studies are suggested. The most desirable particle sizes range from coarse gravel to medium sand (5 to 0.05 mm), with most of the material in the middle range.

6. High-quality limestone is recommended because polluting metals may be present and because, compared to lime ($CaCO_3$), dolomite ($MgCO_3$) is highly insoluble and quite unreactive at field temperatures.

Future Research

1. Future research should be conducted on the effects of soils and leachate variables on specific metal migration so that simulated models can be developed to predict movement of potential pollutants under a wide variety of field disposal conditions.

2. Field studies should be conducted to verify the usefulness of crushed agricultural limestone and should include evaluation of (a) particle size distribution, (b) optimum thickness, (c) cementation characteristics, (d) channeling, and (e) mechanics of placement.

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3. Limestone liners appear to be useful for industrial wastes, but information on this subject is lacking. Research should be undertaken to eliminate the knowledge gap about usefulness of limestone liners for industrial waste disposals.
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SECTION 4

MATERIALS AND METHODS

MATERIALS

Materials used in this study were generally uniform throughout. A few exceptions were required by the nature and time frame of the research, however. For example, leachates were occasionally varied to provide solubility stabilization. Any significant modification of the materials is reported during the discussion of the experimental procedure.

Soils

To avoid organic matter and to more nearly typify the composition of landfill material, nine subsoils representing 7 of the 10 major soil orders were collected throughout the United States. Selected properties of these soils (Table 1) indicate that they range from acid (pH 4.2 for an Ultisol, Wagram sand) to alkaline (pH 7.8 for an Entisol, Anthony sandy loam). The clay varies from 4 to 52% and cation-exchange-capacity (CEC) from 2 to 37 meq/100 g. The clay mineral composition of the <2μ separate varied considerable with no pure species dominating. Yet Anthony sl, for example, contained mostly montmorillonite-like clay minerals and Davidson c and Molokai c contained mostly kaolinite-like clay minerals. The water-saturated soil extract of the soils appear in Table 2 for comparisons. The total Mn, Co, Zn, Ni, Cu and Cr and free Fe oxide levels appear in Table 3 also for comparative purposes.

Leachates

Leachate was generated in three 4,000-liter tanks. Leachate I originated from a concrete septic tank coated inside with epoxy sealant while Leachate II and III came from a steel tank which was also sealed with epoxy. All were packed with representative municipal waste (Table 4), filled with water, and allowed to ferment.

Clear leachate was withdrawn from the bottom of the tank under CO_2 pressure and in the complete exclusion of air as described by Korte et al. (1976a). Because of age of disgestion (3-year difference) the compositions of the two leachates were not the same (Tables 5 and 6). In general, the pH rises with time from acid to near neutral, whereas total organic carbon (TOC), trace and heavy metals, electrical conductivity (EC), soluble salts, and total dissolved solids (TDS) all decrease. Strict municipal solid waste leachate is characteristically low in heavy metals. Consequently the leachates were enriched with the chloride [except for CrVI which was the oxide]

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TABLE 1. GENERAL CHARACTERISTICS OF THE SOILS

Soil Series	Soil Order	Soil Paste pH	Cation Exch Capac., meq/100g	Elec. Cond.of Extract, µmhos/cm	Column Bulk Density, g/cc	Column Porosity g/cm^3	Silt %	clay	Soil Surface Area m^2/g	Predominant Clay Minerals *
Davidson	Ultisol	6.4	9	169	1.40	0.476	20	52	51.3	Kaolinite
Molokai	Oxisol	6.2	14	1262	1.44	0.429	25	52	67.3	Kaolinite, gibbsite
Nicholson	Alfisol	6.7	37	176	1.53	0.460	47	49	120.5	Vermiculite
Fanno	Alfisol	7.0	33	392	1.48	0.484	19	46	122.1	Montmorillonite, mica
Mohave (Ca)	Aridisol	7.8	12	510	1.54	0.446	28	40	127.5	Mica, montmorillonite
Ava	Alfisol	4.5	19	157	1.45	0.478	60	31	61.5	Vermiculite, kaolinite
Chalmers	Mollisol	6.6	26	288	1.60	0.476	58	31	95.6	Montmorillonite, vermiculite
Anthony	Entisol	7.8	6	328	2.07	0.360	14	15	49.8	Montmorillonite, mica
Mohave	Aridisol	7.3	10	615	1.78	0.365	37	11	38.3	Mica, kaolinite
Kalkaska	Spodosol	4.7	10	237	1.53	0.404	4	5	8.9	Chlorite, kaolinite
Wagram	Ultisol	4.2	2	225	1.89	0.378	8	4	8.0	Kaolinite, chlorite

*Listed in order of dominance

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TABLE 2. SOME CHEMICAL CHARACTERISTICS OF WATER-SATURATED PASTE EXTRACTS OF SOILS STUDIED

Soil Series and Texture Class	Cations (ppm)				Anions (ppm)						Trace Metals (ppm)	
	K	Na	Ca	Mg	HCO_3	Cl	SO_4	NO_3	P	Si	Fe	Mn
Wagram s	135	7	12	1	10	1	60	6	0.1	4	0.04	0.060
Ava si c l	7	4	6	5	10	49	15	0.2	0.1	18	0.04	0.005
Kalkaska s	27	7	17	3	24	6	20	0	0.1	13	0.40	0.020
Davidson c	6	4	13	4	13	12	40	9	0.1	2	0.04	0.001
Molokai c	144	68	62	41	26	1	60	3	0.2	21	0.30	0.003
Chalmers si c l	4	6	15	5	24	6	40	2	0.2	5	0.05	0.001
Nicholson si c	15	37	7	2	32	10	15	1	0.1	40	0.04	0.001
Fanno c	36	20	30	8	120	6	16	1	0.1	8	0.04	0.001
Mohave s l	66	55	54	9	98	10	17	28	0.4	23	0.04	0.001
Anthony s l	76	16	46	8	111	4	12	2	0.4	13	0.32	0.005

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TABLE 3. TOTAL ANALYSIS OF SOILS FOR TRACE METALS AND FREE IRON OXIDES

Soil Series and Texture Class	Trace Metals (µg/g)						Fe Oxides (%)
	Mn	Co	Zn	Ni	Cu	Cr	
Wagram s	50	bdl*	40	80	62	bdl	0.6
Ava si c l	360	50	77	110	80	55	4.0
Kalkaska s	80	25	45	50	46	15	1.8
Davidson c	4100	120	110	120	160	90	17.0
Molokai c	7400	310	320	600	260	410	23.0
Chalmers si c l	330	60	100	130	83	68	3.1
Nicholson si c	950	50	130	135	65	68	5.6
Fanno c	280	45	70	100	60	38	3.7
Mohave s l	825	50	85	100	265	18	1.7
Mohave c l	770	50	120	120	200	40	2.5
Anthony s l	275	50	55	80	200	25	1.8

*Below detectable limit.

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TABLE 4. COMPOSITION OF SOLID WASTE USED TO GENERATE LEACHATE

Waste Constituent	Amount Loaded in 4,000-liter Generator (lb)	(%)
Paper (mostly newspaper)	1,400	45.7
Food waste	450	14.7
Garden waste	376	12.3
Plastic	34	
Rubber	109	
Leather	60	
Textiles	109	
Total	312	10.2
Metal (mostly cans)	187	6.1
Glass	177	5.8
Ash	59	
Soil	68	
Total	127	4.1
Calf manure	35	1.1

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of the heavy metal of interest to provide ~ 100 mg/liter. These metals are usually complexed when in natural systems including the natural MSW leachates used here. This concentration, which might be found in some mixed municipal-industrial and industrial waste leachates during the early period of deposition and biodegradation (Chian and DeWalle, 1977; Garland and Mosher, 1975; Brunner and Keller, 1972; Walker, 1969) was necessary to assure that migration would occur through the soil column. Where enrichment leachates were used, they were allowed to stand and incubate for several days until the soluble concentration of the heavy metal had stabilized at a known level. During collection and infiltration of the soil columns, the leachate continuously remained under a CO_2 bubbling system (Fuller, 1978) and was monitored daily for certain common metals such as Fe, Ca, Mg, Na, and K, and pH, TOC, and EC.

The 100-mg/liter concentration was believed to be necessary to have sufficient soluble metal to assure migration through the soil columns in a workable period of time and yet achieve breakthrough (C/C_o = 1.0; where C = concentration in effluent and C_o = concentration of influent). Breakthrough is necessary for predictive migration modeling. Constituent concentration in MSW leachate does not remain at stable soluble levels for long periods of time because of the biological nature of the waste (Tables 5 and 6). Data for MSW Leachate III are not given because of the similarity with Leachate II. Variability in TOC, dissolved solids (EC), soluble inorganic salts, Fe, and pH, for example, influences soil attenuation of heavy metals and their solubility in the leachate (O'Donnell et al., 1977; Fuller, 1977a, b). The aim is to avoid the effects of these and other changes as much as possible.

Before adopting the enrichment procedure, a study was made to evaluate the effects of heavy metal concentration on attenuation. It was found that the attenuation was proportional to the concentration of the heavy metal in solution and breakthrough (C/C_o = 1) occurred after about the same number of pore volume displacements (data presented in the discussion). Young (0- to 3-year) MSW leachates contain higher concentrations of many diverse soluble constituents than older leachates (> 3 years). Relative levels of added Cd (< 100 mg/liter, data presented in the text) may be so small and competitive as not to behave as one might suspect as in cation exchange reactions in natural dilute soil solutions. These reactions certainly require additional study before we speculate further. Flux comparisons therefore should be held to a single heavy metal at a time, except where concentrations (ppm and molarity) of Fe, Ni, and Cr, and V or Cu and Zn fall near to each other, Alesii et al. (1980).

Limestone

Unsieved, commercial-grade limestone (98% $CaCO_3$) from Cedar Bluff, Kentucky, was used. The limestone was developed for commercial agricultural soil application. It has a particle density of 2.72 g/cm^3 and a fairly broad range of size distribution, Table 7. Particle size distribution of two other high-quality commercial agricultural limestones are included in the table for purposes of comparison. When used as a leachate barrier, the Cedar Bluff limestone was compacted to an average density of 1.67 g/cm^3.

TABLE 5. SOME CHEMICAL CHARACTERISTICS OF LEACHATE I (CONCRETE GENERATOR)

Sampling Date	pH	EC mmhos/cm	TOC	Ca	Mg	Na	K	NH_4-N	P	Si	Cr	Cu	Fe	Mn	Ni	Zn
				ppm												
11/29/73	6.4	3.2	500	168	60	74	1900	90	2	35	0.10	0.30	100	2.0	0.20	0.8
12/20/73	6.4	3.5	490	172	59	98	1900	84	2	31	0.10	0.10	100	2.0	0.10	0.5
1/9/74	6.4	3.5	500	170	60	100	1900	100	2	25	0.10	0.10	107	2.2	0.10	1.0
2/8/74	6.5	3.5	450	155	45	120	2050	150	1	25	bdl	bdl	97	1.8	0.10	2.1
3/22/74	6.6	3.6	480	150	40	100	1650	180	1	20	bdl	bdl	100	1.8	bdl	1.7
4/9/74	6.6	3.6	480	175	53	115	900	154	2	23	bdl	bdl	105	1.8	bdl	0.6
5/23/74	6.5	3.5	490	200	41	110	900	133	1	19	bdl	bdl	70	1.7	bdl	0.7
6/27/74	6.4	3.5	390	180	50	135	850	173	1	20	bdl	bdl	80	0.9	bdl	0.4
7/25/74	6.4	3.6	350	160	50	150	900	190	8	21	bdl	bdl	70	0.9	bdl	0.4
8/13/74	6.5	3.4	3[illegible]	160	45	120	900	124	1	20	bdl	bdl	70	0.9	bdl	0.6
9/17/74	6.4	3.4	300	140	45	86	950	124	1	20	bdl	bdl	55	0.6	bdl	0.4
10/31/74	6.4	3.3	310	150	30	75	200	110	1	20	bdl	bdl	68	0.7	bdl	0.5
11/20/74	6.5	3.2	280	160	40	75	200	100	1	20	bdl	bdl	63	0.7	bdl	0.6
12/2/74	6.6	3.0	210	140	30	90	180	90	1	20	bdl	bdl	69	0.7	bdl	0.6
2/2/75	6.6	2.6	190	123	30	100	170	54	3	20	bdl	bdl	80	0.8	bdl	0.6
4/18/75	6.6	2.6	160	143	25	91	150	55	1	14	bdl	bdl	90	1.0	bdl	0.6
5/20/75	6.4	2.6	150	163	40	90	200	68	5	31	bdl	bdl	120	1.0	bdl	1.0
6/27/75	6.2	2.8	150	125	40	100	280	nd	1	24	bdl	1	63	0.6	bdl	0.2
7/28/75	6.4	2.8	200	190	38	110	108	nd	5	20	bdl	1	57	0.6	bdl	0.3
8/28/75	6.4	2.8	200	198	38	110	108	nd	1	21	bdl	bdl	50	1.0	bdl	0.6
9/17/75	6.4	2.9	200	210	48	110	300	nd	2	20	bdl	bdl	86	1.3	bdl	2.2

* Below detectable limits of the atomic absorption method used. The detectable limits for the atomic absorption method used, in µg/l, are: Cd = 0.005, Cr = 0.05, Co = 0.05, Pb = 0.5, Ni = 0.05, Mn = 0.05, Zn = 0.005, Al = 0.5, Cu = 0.05, and Fe = 0.05.

TABLE 5. (Continued)

Sampling Date	ph	Ec	TOC	Ca	Mg	Na	K	NH_3-N	P	Si	Cr	Cu	Fe	Mn	Ni	Zn
		mmhos/cm	ppm													
10/27/75	6.4	2.8	190	155	33	60	235	nd	2	19	bdl*	bdl	90	1.3	bdl	0.3
12/18/75	6.4	2.8	180	130	30	60	220	nd	3	14	bdl	bdl	80	1.3	bdl	0.8
1/2/76	6.4	2.7	170	155	48	60	210	nd	2	13	bdl	bdl	70	1.1	bdl	0.7
2/21/76	6.4	2.6	180	172	21	72	198	nd	1	15	bdl	bdl	44	1.2	bdl	0.6
4/28/76	6.4	2.5	130	153	51	55	200	nd	3	12	bdl	bdl	40	0.6	bdl	0.1
5/27/76	6.4	2.5	110	148	48	68	204	nd	2	13	bdl	bdl	41	1.0	bdl	0.2
6/29/76	6.4	3.1	134	150	40	67	180	nd	2	15	bdl	bdl	44	0.6	bdl	0.2
7/27/76	6.4	3.2	194	185	39	56	200	nd	2	16	bdl	bdl	31	0.6	bdl	0.4
8/17/76	6.4	3.4	125	185	38	58	200	nd	3	16	bdl	bdl	37	0.3	bdl	0.2
9/27/76	6.4	3.0	142	170	36	56	180	nd	3	17	bdl	bdl	42	0.6	bdl	0.1
10/20/76	6.4	2.0	165	140	20	70	168	nd	3	16	bdl	bdl	41	0.5	bdl	0.1
12/1/76	6.5	2.0	116	153	20	70	125	nd	2	15	bdl	bdl	42	0.6	bdl	0.1
2/8/77	6.4	1.9	140	168	20	65	115	nd	3	16	bdl	bdl	40	0.7	bdl	0.50
3/21/77	6.4	1.7	160	122	14	84	119	nd	2	14	bdl	bdl	40	0.7	bdl	0.70
5/17/77	6.4	1.6	190	133	15	75	130	nd	2	12	bdl	bdl	71	0.7	bdl	0.48
6/24/77	6.4	1.6	210	125	15	63	125	nd	3	16	bdl	bdl	71	0.7	bdl	0.36
7/25/77	6.2	1.8	280	119	21	85	140	nd	2	15	bdl	bdl	71	0.5	bdl	0.20
8/22/77	6.4	1.8	300	131	25	89	146	nd	2	14	bdl	bdl	53	0.5	bdl	0.28

* bdl -- below detectable limits of the atomic absorption method used. The detectable limits for the atomic absorption method used, in µg/l, are: Cd = 0.005, Cr = 0.05, Co = 0.05, Pb = 0.5, Ni = 0.05, Mn = 0.05, Zn = 0.005, Al = 0.5, Cu = 0.05, and Fe = 0.05.

TABLE 6. SOME CHEMICAL CHARACTERISTICS OF LEACHATE II (STEEL GENERATOR)

Sampling Date	pH	EC	TOC	Common Elements						Trace and Heavy Metals								
		mmhos/cm	----------	Ca	Mg	Na	K	P	Si	Cd	Co	Cr	Cu	Fe	Mn	Pb	Ni	Zn
										ppm								
10/23/75	3.8	8.5	25,000	1,300	450	750	1,550	20	35	0.45	0.3	2.4	0.70	830	7	1.8	0.90	165
10/28/75	4.8	9.0	19,000	1,100	360	700	1,600	18	25	0.40	0.3	2.4	0.60	670	8	3.3	0.55	110
11/5/75	4.9	9.5	17,000	1,100	270	650	1,300	16	33	0.25	0.2	0.8	0.25	670	12	1.5	0.60	95
12/18/75	5.0	15.1	17,100	1,150	270	650	1,250	19	35	0.20	0.2	0.5	0.25	600	15	bdl	0.60	20
1/2/76	5.0	14.0	17,200	2,050	310	500	1,250	20	33	0.20	0.2	0.4	0.25	650	16	bdl	0.60	20
1/22/76	5.0	12.5	17,200	1,710	180	720	1,710	18	38	0.10	0.2	0.4	0.10	700	16	bdl	0.55	19
2/19/76	5.0	13.0	16,000	1,640	176	760	1,630	19	36	bdl *	0.2	0.4	bdl	875	16	bdl	0.50	16
2/26/76	5.0	13.5	14,600	1,660	176	680	1,630	25	36	bdl	0.2	0.3	bdl	875	16	bdl	0.40	14
3/22/76	5.0	14.0	14,300	1,730	420	720	1,600	33	36	bdl	0.2	0.2	bdl	800	14	bdl	0.50	12
4/27/76	4.8	14.0	15,300	1,740	450	670	1,660	20	36	bdl	0.4	0.2	bdl	880	14	bdl	0.10	6
5/27/76	4.6	14.0	14,300	1,040	450	640	1,130	18	37	bdl	0.6	0.2	bdl	960	16	bdl	0.10	4
6/2/76	4.6	14.0	12,525	990	360	540	880	18	36	bdl	0.5	0.2	bdl	860	13	bdl	0.10	3
6/27/76	4.7	14.0	12,200	950	360	510	950	9	35	bdl	0.5	bdl	bdl	820	14	bdl	0.10	3
7/19/76	5.3	17.0	13,300	750	370	460	1,160	11	36	bdl	0.6	bdl	bdl	750	15	bld	0.75	2
7/27/76	5.3	17.0	13,010	800	360	440	1,120	12	37	bdl	0.6	bdl	bdl	840	14	bdl	0.75	3
8/29/76	5.4	17.0	11,600	820	310	420	1,060	12	33	bdl	0.6	bdl	bdl	890	13	bdl	0.70	7
9/27/76	5.4	11.5	10,100	815	270	370	980	16	36	bdl	0.6	bdl	bdl	900	12	bdl	0.70	8
10/20/76	5.4	9.0	7,600	690	100	300	700	12	33	bdl	0.5	bdl	bdl	640	12	bdl	0.50	6
11/8/76	5.4	9.0	7,500	735	110	300	700	12	26	bdl	0.5	bdl	bdl	720	12	bdl	0.25	7
12/1/76	5.4	9.5	7,400	760	110	310	700	12	33	bdl	0.4	bdl	bdl	720	13	bdl	0.25	8
1/14/77	5.4	9.5	7,800	760	110	300	680	12	32	bdl	0.4	bdl	bdl	720	13	bdl	0.25	9
2/8/77	5.4	9.1	7,900	665	110	300	670	12	33	bdl	0.4	bdl	bdl	790	13	bdl	0.25	9
3/21/77	5.4	9.1	7,500	690	100	310	640	12	32	bdl	0.9	bdl	bdl	880	9	bdl	0.25	14
5/3/77	5.4	9.1	7,500	750	200	340	660	12	33	bdl	0.9	bdl	bdl	990	9	bdl	0.25	14
6/27/77	5.4	9.8	7,800	790	190	340	700	12	32	bdl	0.9	bdl	bdl	1,010	10	bdl	0.50	13
7/25/77	5.5	10.2	8,700	820	180	350	720	12	33	0.1	0.8	bdl	bdl	1,380	12	bdl	0.80	13
8/22/77	5.4	10.1	7,800	790	200	350	690	12	33	0.1	0.9	bdl	0.1	1,300	11	bdl	0.50	12

*Below detectable limits

Table 6 (continued)

Sampling Date	pH	EC mmhos/cm	TOC	Ca	Mg	Na	K	P	Si	Cd	Co	Cr	Cu	Fe	Mo	Pb	Ni	Zn
									ppm									
8/3/77	5.7	10.0	7,531	752	149.5	360	576	12	33	T†	1.10	-	T	1,383	10.3	0.8	.52	6.10
9/31/77	5.9	9.9	8,800	714	137.4	395	8	12	33	.01	1.10	-	T	1,220	8.6	0.8	.6	3.95
10/3/77	5.3	8.8	3,100	368	128.4	372	542	12	33	T	0.50	-	T	555	2.8	0.62	.05	0.90
11/13/77	6.7	8.8	2,925	444	150	360	584	2	40	T	0.34	-	T	339	0.61	bdl	-	0.66
1/24/78	6.8	8.0	2,750	540	147	366	582	2	40	T	0.34	-	T	439	0.61	bdl	.05	0.77
2/15/78	6.7	5.0	2,188	406	106	310	1,797	2	41	T	0.34	-	T	408	2.50	bdl	.21	0.80
3/15/78	6.7	5.0	2,	303	103	319	1,760	2	-	.03	<.02	-	.08	250	1.68	0.12	<.05	1.00

† Trace

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TABLE 7. PARTICLE SIZE DISTRIBUTION OF AGRICULTURAL LIMESTONE FROM THREE KENTUCKY SOURCES

φ	mm	USDA	Lexington (%)	Cedar Bluff (%)	Gibsonburg (%)
-2.5 to -2.0	-5.66	Gravel	0.9	0	0
-2.0 to -1.5	5.66-2.80	Gravel	17.3	5.1	0
-1.5 to -1	2.80-2.00	Gravel	13.2	4.4	0
-1 to -0.5	2.00-1.40	Very coarse sand	15.2	6.8	0
-0.5 to 0	1.40-1.00	Very coarse sand	15.2	6.8	0
0 to 0.5	1.00-0.71	Coarse sand	10.2	8.3	0
0.5 to 1	0.71-0.50	Coarse sand	7.5	9.4	0
1 to 1.5	0.50-0.355	Medium sand	8.3	12.5	0.3
1.5 to 2.0	0.355-0.250	Medium sand	6.0	10.2	0.4
2.0 to 2.5	0.250-0.180	Fine sand	3.0	6.7	1.4
2.5 to 3.0	0.180-0.125	Fine sand	2.4	6.3	6.8
3.0 to 3.5	0.125-0.090	Very fine sand	1.5	4.8	13.3
3.5 to 4.0	0.090-0.063	Very fine sand	1.0	6.0	13.5
- - -	0.06-0.050	Very fine sand	0.8	1.9	24.7
- - -	< 0.050	Silt and clay	1.2	9.9	39.5

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Pecan Hulls

Pecan hull waste from a local commercial pecan production enterprise was further crushed by hand in a ceramic mortar to pass a 2 mm sieve. It was used in this form to layer over soil in a column as a pollution migration barrier.

Hydrous Oxides of Iron

Iron rust was scraped from a gas boiler, ground in a steel mortar to pass a 0.5 mm sieve, and used without further alteration. No carbon was identified as a contaminant.

METHODS

Methods were kept uniform throughout the study. Details of the materials and methods used in this research are described fully elsewhere (Fuller, 1977a, b and 1978; Korte et al., 1975 and 1976a, b; Alesii et al., 1980; Fuller et al., 1979a, b).

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Leachate Generator

Leachate generators consisted of two 4,000-liter tanks. Generator I was a home-owner-type septic tank coated with epoxy sealant, and generators II and III were identical steel tanks.

Soil Columns

Preparation of the soil columns for attenuation evaluation followed the procedure described previously for all the heavy metal migration research (Korte et al., 1976a, c and Fuller, 1978a). The 10 or 20 cm of soil were uniformly packed into two sizes of PVC cylinders measuring 10 by 22 and 5 by 12 cm to form columns of known bulk densities shown in Table 1. The upper 2 cm of each column were packed with quartz sand to prevent plugging. MSW leachate was perfused through soil using a Pharmica peristaltic pump regulated to deliver fixed fluxes ranging from 1 to 14 ml/hour. The effluents were collected for Al, As, Be, Cd, Cr, Fe, Ni, Se, V, and Zn each hour by use of a fraction collector.

Solute (influent leachate) movement in soil columns is variable in nature (O'Donnell et al., 1977). Precise replication of data from such experiments is infrequently achieved. Soil packing, irregular and irreproducible pore geometry, and trapped gases are uncontrolled variables that can account for slight variations in experimental breakthrough curves despite rigid adherence to standardized packing technique. The ability to reproduce data from column experiments, therefore, was undertaken.

Columns (5 by 10 cm) of nine soils were leached under saturated anaerobic steady-state conditions against gravity with 100 ppm Cd in solution and with natural MSW Leachates I, II and III. The error estimates from these studies were found to be about 3% (O'Donnell, et al., 1977; Alesii et al, 1980). Since Ni and Zn gave similar results, the data are not shown. The

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experimental error in all subsequent column studies, therefore, was assumed to be 3%. In the few instances where experimental soil columns appeared to become erratic, they were discarded and replaced by new, repacked columns.

All data are plotted as C/C_o vs. pore volumes (time) where C/C_o is the ratio of effluent concentration to influent concentration. When $C/C_o = 1.0$, this is called breakthrough, Figure 2. MSW leachate was passed through the soil columns until one of three conditions was met: (i) breakthrough, (ii) steady state (unchanging or very slowly changing) effluent concentration at value below that of influent, or (iii) continued absence of the element after leaching for prolonged periods of time. The data plotted in the flux breakthrough curves are from representatives of individual soil columns, not averages. A minimum of 21 concentration points were used to establish flux curves for sand soils, whereas up to 10 times as many were used for the more retentive clay and silty clay loams having slower rates of metal migration. Since metal concentration was monitored on an hourly basis, there was adequate opportunity for a large number of reference points. Data in the tables, which were taken into consideration in the statistical analyses, represent values from more than one soil column.

The selection of 10-cm length for the soil columns was based on numerous recently published studies showing the achievement of a long-term or steady-state velocity occurring at approximately 10 cm (Fuller et al, 1979a), Figure 3.

Preliminary soil-column experiments also were undertaken to evaluate flux effects as influenced by different soil bulk densities using displacing solutions other than the MSW leachates. These were (i) aqueous H_2SO_4 adjusted to pH 3.0; (ii) 0.025M $AlCl_3$, plus 0.025M FeCl; with enough HCl added to attain a pH of 3.0; and (iii) deionized water. For example, Nicholson sic was packed into two sets of columns at fixed bulk densities of 1.53 and 1.75 g/cm^3. Flow rate in the lower bulk density column was maintained at 0.5 PV/24 hours and the other at 0.1 PV/24 hours. Data from the $AlCl_3$-$FeCl_2$ solutions were expected to provide information on the effects of a very strongly buffered acid and a readily oxidizable leachate. This should represent a maximum contribution from soil in contact with certain industrial waste streams (e.g., waters from abandoned coal mines).

Batch Techniques

The effect of acidification, aeration by air, and by pure CO_2 only, on the solubility of Fe and Mn of natural leachate was studied. Leachate I was collected under two sets of conditions, (a) a strict CO_2 atmosphere, and (b) the natural atmosphere. Each set contained 0, 1, and 5 percent HCl. Component solubility was evaluated on the solution passing through a standard 0.45-μ millipore filter as used for water analyses, U.S. EPA (1976).

The effects of time of aeration by air only and by pure CO_2 only on the solubility of As, Be, Cd, Co, Cr, Cu, Hg, Ni, PB., Se, V, and Zn spiked at 100 mg/l, in a soluble condition, into Leachate II were studied using a simplified batch technique. Air or CO_2 was bubbled through the solutions at a constant rate of 60 ml/min for periods of 0, 4, and 72 hours. Again, the

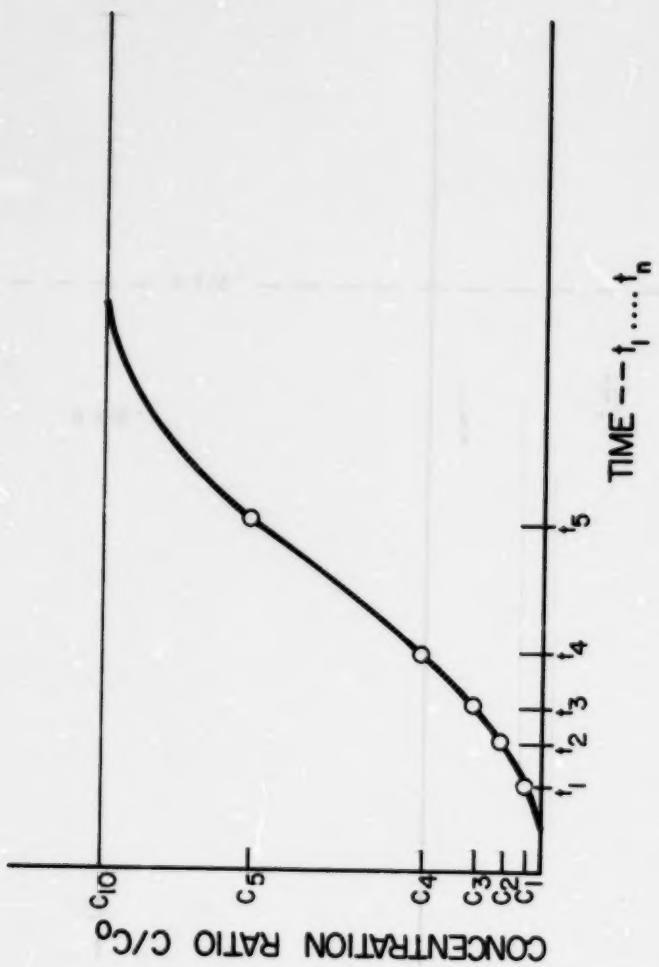

Figure 2. Ratio of effluent concentration to influent concentration (C/Co; where C/Co = 1 is breakthrough) plotted against time (or pore volume displacement).

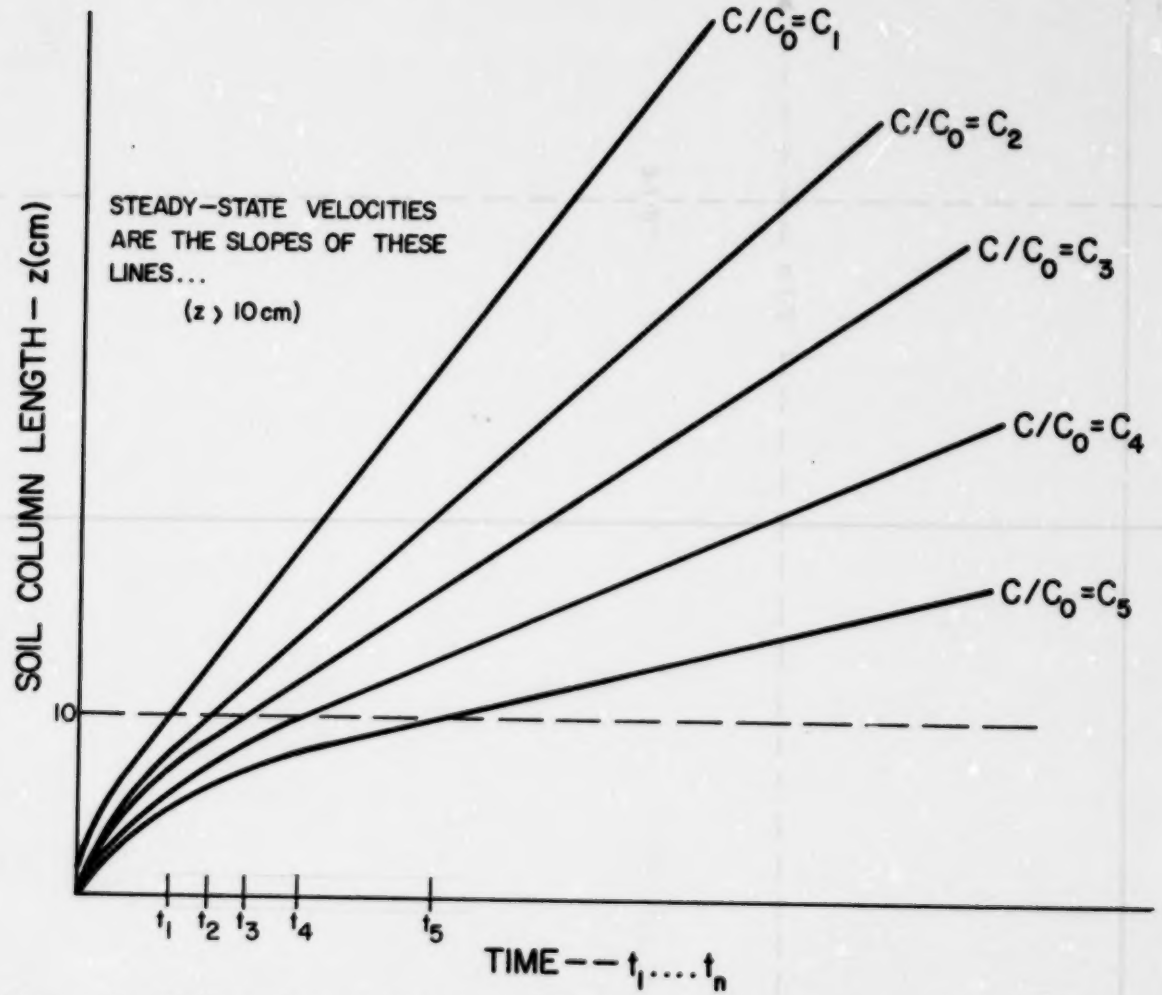

Figure 3. Trajectaries of different relative concentrations. (Plot of Z = Z(t), where Z = (Zt) satisfied $C(t,z(t)) = C_1$, i - 1, 2, 3, 4, 5.

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solutions were passed through a 0.45-μ filter under conditions of the experiment and the soluble constituents analyzed.

Leachate II samples were diluted with deionized H_2O in ratios of 0:1, 1:1, and 1:2, stepwise acidified at pH increments of 0.5 from the natural pH of 5.4 to 2.0 and placed in a slow-speed shaker under CO_2 for periods up to 72 hrs. The solubility of Cr, Fe, TOC, and total dissolved solids (TDS) as influenced by pH, aqueous dilution, and time of contact was determined on the < 0.45-μ filtrate as described.

Chemical Analyses

Free oxides of the soils were determined by the method of Kilmer (1960), surface area by the method of Heilman et al. (1965) using the ethylene glycol monoethyl ether technique, and manganese by modified procedure of Bernas (1968). For total analysis, a sample size of 0.1 g of finely ground soil, 1 ml of aqua regia, and 6 ml of HF were used for digestion. Boric acid (2.0 g) then was added and the sample diluted to a final volume of 50 ml. The pH values were measured using the glass electrode. Where pH, common ions, total dissolved solids, and cation exchange capacity were evaluated, the methods recommended by the USDA (Richards, 1954) were used. Standard X-ray (Jackson, 1963) and mechanical analysis procedures (Day, 1965) were used to identify the < 2μm clay minerals and the particle-size distribution of the soils. Texture classes are tabulated in Table 1.

The singly enriched elements (As, Be, Cd, Cr, Ni, Se, V, and Zn) and the natural elements Al, Fe, and Mn contained in the MSW Leachates I, II and III (influents) and soil column effluents were measured by atomic absorption spectrophotometry using standard procedures recommended for the 810 Jarrell-Ash atomic unit. Chemical interferences were minimized by matrix adjustment using La and K according to Ando et al. (1969). Using the dual channel of the AA with one channel carrying a hydrogen continuum lamp, we evaluated extent of background for Cd. Background corrections were found not to be required because of the comparatively low interferences in diluted leachate as compared with the digestion in redistilled conc. HNO_3. All samples were collected in the presence of redistilled HNO_3 to give a final pH of 2. The first pore volume displacement was discarded because it represented the deionized water used to saturate the soil column. The Ca, Mg, K, and Na were measured by flame emission (USEPA, 1974) and NH_4-N, P, and Si according to the conventional methods required by USEPA (1974) water and waste water methods.

Total organic carbon (TOC) was determined by a Beckman 915 A Model Total Organic Carbon Analyzer.

Hexavalent CrVI values were obtained by the colorimetric Standard Methods for the Examination of Water and Waste Water (1975). The trivalent CrIII was considered to be the difference between hexavalent CrVI and total Cr [CrIII + CrVI].

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SECTION 5

RESULTS AND DISCUSSION

LEACHATE VARIABLES AFFECTING METAL MOVEMENT FROM LANDFILLS

Municipal solid waste (MSW) leachates are not unlike most other organic-inorganic aqueous systems, since they share the characteristics of a dynamic biological brew that undergoes changes continuously. The kind and magnitude of these changes may be expected to influence the solubility and form of the constituent in the leachate. The way the potential pollutant reacts with the soil, therefore, also is expected to vary with leachate composition changes. Variation in the composition of the MSW leachate is most pronounced during the first few years of waste deposition. These variations were found (Fuller, 1977a, and Fuller et al., 1979a, b) to be:

1. pH rises from ~ 3.5 to 7.0.

2. Oxidation-reduction potential rises from a low of about 60 to 150 Eh.

3. Sulfide rises severalfold.

4. Sludge formation tendency rises greatly with time.

5. Free, volatile acid decreases from a maximum about 10-fold.

6. Total organic carbon decreases about 100-fold, COD decreases many-fold with time, roughly following TOC content.

7. Electrical conductivity decreases severalfold.

8. Soluble heavy metal concentration decreases rapidly with time (often completely disappearing from detection).

9. Soluble Fe decreases as much as 5-fold.

10. Soluble P decreases several-fold.

11. Common soluble ions (Ca, Mg, Na, K, Cl, SO_4, for example) decrease markedly.

Common salts listed in item 11 decrease but do not disappear. They accumulate primarily in the sludge solids as precipitates and adsorbates on the solid waste surfaces, and penetrate the site-enveloped soils (Fuller et al., 1979a). Since most of the above constituents appear to influence the rate

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of pollutant migration, any prediction of certain heavy and trace metal behavior must include the impact of leachate aging (Fuller et al., 1979a, b, c).

Effect of Aeration with O_2 and CO_2

One of the first MSW leachate variables to be identified was its color change as the solution was withdrawn from the solid waste deposit (Korte et al., 1976a; Fuller, 1978). Leachate collected without acid (HCl or HNO_3) or under a CO_2 atmosphere turned from pale straw color to dark green to black within seconds after being exposed to the atmosphere. Not only were precipitates formed that contained metals in measurable quantities (such as Fe and Mn), Table 8, but the pH was affected. The pH change was experimentally confirmed by aerating freshly drawn leachate samples rapidly over a period of 30 minutes, Figure 4. The pH rose parabolically from 6.4 to 8.8. Aeration of the same Leachate I with CO_2 alone did not modify the original pH of 6.4 during the same period of time. Further research with other MSW leachates established a general pattern of metal solubility behavior as a result of exposure to pure CO_2 and/or O_2.

TABLE 8. EFFECT OF EXPOSURE TO AIR, CO_2, AND ACIDIFICATION ON THE Fe AND Mn SOLUBILITY OF SOLID WASTE LEACHATE I.

Treatment of Leachates	Recovery	
	Fe (%)	Mn (%)
Sampled with CO_2, 0% HCl	95	90
Sampled with CO_2, 1% HCl	99	95
Sampled with CO_2, 5% HCl	99	99
No CO_2, no acid*	52	40
No CO_2, 1% HCl*	98	80
No CO_2, 5% HCl*	99	99
No CO_2, 0.1% HNO_3*	90	83

* Samples all filtered (< 0.45μ) the day after collection.

A batch study was undertaken in which certain metals (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn) were enriched in Leachate II singly at 100 mg/l. Where possible, the appropriate chloride was used for the enrichment. Oxides were used for As, Cr, V, and Se, and nitrate for Pb. The oxidation states for the elements were As^{+3}, Be^{+2}, Cd^{+2}, Cr^{+3}, Cu^{+6}, Hg^{+2}, Ni^{+2}, Pb^{+2}, Se^{+4}, and V^{+5}. Aeration procedure was as follows: (a) set #1 was bubbled with CO_2 for 48 hrs after enrichment with the element, (b) set #2 was bubbled with air for 48 hrs after enrichment with the element, and (c) set #3

was bubbled with air for 48 hrs before enrichment with the element. After 48-hr treatments, the solutions were centrifuged, passed through a < 0.45μ filter, and the clear supernatant analyzed, Table 9.

Aeration of the natural Leachate II, which was relatively high in constituents and at a pH of 5.2, resulted in observable precipitate of organic matter (TOC) and Fe. These changes occurred without change in pH. Various alterations in soluble levels of the 12 enriched elements occurred also, as shown by data in Table 9. Aeration with air seemed to result in a greater or about the same precipitation of the metals when performed after the enrichment of the element than before, except for Hg. At pH 5.2, Cr, Hg and Pb appeared to precipitate readily from solution regardless of aeration sequence.

The stability of the pH at 5.2 despite aeration for 48 hours was difficult to understand since Leachate I was so susceptible to pH changes from aeration. The differences in titrable acidity which favored Leachate II were attributed to differences in aeration rates. Leachate I of pH 6.4 as reported in Figure 3 was aerated three times faster than Leachate II in this experiment.

Effects of Aqueous Dilution and pH

Solid waste landfills generate leachates as a consequence of rainfall, either directly or as seepage into the disposal cells. The amounts of water that accumulated in the landfills varies with rainfall distribution and intensity. Experiments were designed, therefore, to provide some evaluation of this variable diluting circumstance.

The concentration of certain constituents in MSW leachate was found to influence the migration rate of Cd through Ava sicl (Figure 5). Attenuation of Cd was greater in water alone and in diluted leachate than in the natural leachate. Moreover, the older the leachate (and thus the more dilute with respect to all constituents, including TOC), the greater was the retention of Cd by the soil. This result suggests that leachates in MSW landfills contain certain constituents that enhance the migration rate of Cd through the soil by interfering with those mechanisms (or reactions) that are responsible for attenuation of the element when Cd is present in water alone.

This observation suggests a basic principle for leachate management in land disposal programs: Mixing a waste that produces leachate containing high levels of constituents with one that produces low levels will either enhance or restrict pollutant migration more than if they were disposed of separately. Whether migration is enhanced or restricted depends on the respective compositions of the two leachates. For example, if Cd occurred in a leachate high in TOC, salts, etc., its migration would probably be less rapid if the leachate were diluted with some other aqueous disposal solution or rain water. On the other hand, if Cd were contained in a dilute leachate, mixing it with a more concentrated leachate would accelerate its rate of migration through soil. This principle may be particularly helpful in the joint management of municipal and industrial disposals whose leachates are likely to vary widely from each other with regard to concentration of

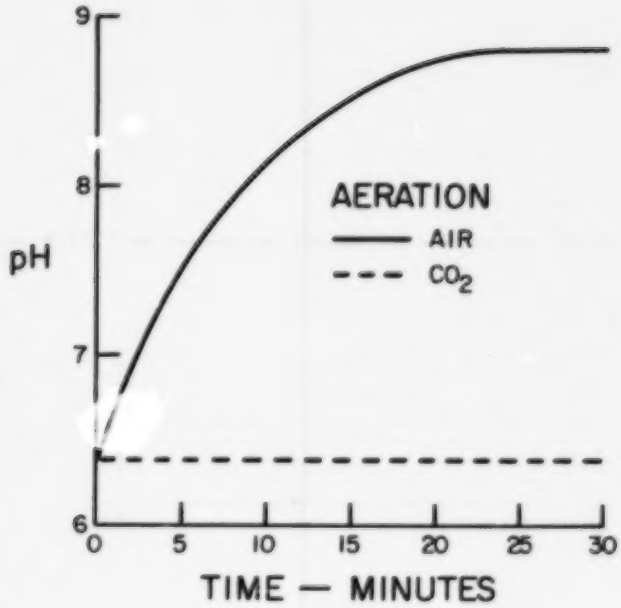

Figure 4. Effect of aeration on the pH of municipal solid waste Leachate I.

TABLE 9. EFFECT OF AERATION WITH CO_2 AND AIR ON THE SOLUBILITY OF 12 TRACE ELEMENTS ENRICHED SINGLY TO MUNICIPAL SOLID WASTE LEACHATE II

Element Added*	Element Remaining in Solution (ppm)	Supernatant Characteristic pH	Fe (ppm)	TOC (%)
	Bubbled with CO_2 for 48 hr after enrichment of element			
Blank	---	5.2	750	1.00
As	100	5.1	390	0.61
Be	95	5.2	290	0.64
Cd	95	5.2	708	--
Co	95	5.2	707	--
Cr	8	5.2	460	--
Cu	84	5.2	675	--
Hg	18	5.2	175	0.62
Ni	67	5.2	682	--
Pb	37	5.2	679	--
Se	76	5.2	160	0.71
V	95	5.2	750	0.65
Zn	67	5.2	707	--
	Bubbled with air for 48 hr after enrichment of element			
Blank	---	5.2	750	1.00
As	57	5.2	130	0.62
Be	84	5.2	175	0.55
Cd	85	5.2	152	0.57
Co	86	5.2	169	0.59
Cr	3	5.2	118	0.59
Cu	80	5.2	17	0.61
Hg	(40)	5.2	75	0.56
Ni	57	5.2	186	0.70
Pb	15	5.2	152	0.60
Se	32	5.2	70	0.62
V	33	5.2	50	0.64
Zn	67	5.2	161	0.58
	Bubbled with air for 48 hr before enrichment with element			
Blank	---	5.2	750	1.00
As	100	5.2	36	0.63
Be	82	5.2	27	0.55
Cd	84	5.2	207	0.64
Co	86	5.2	243	0.85
Cr	12	5.2	51	0.57
Cu	83	5.2	159	0.57
Hg	13	5.2	27	0.58
Ni	62	5.2	275	0.58
Pb	15	5.2	243	0.50
Se	42	5.2	27	0.46
V	95	5.2	27	0.59
Zn	70	5.2	222	0.39

* 100 ppm.

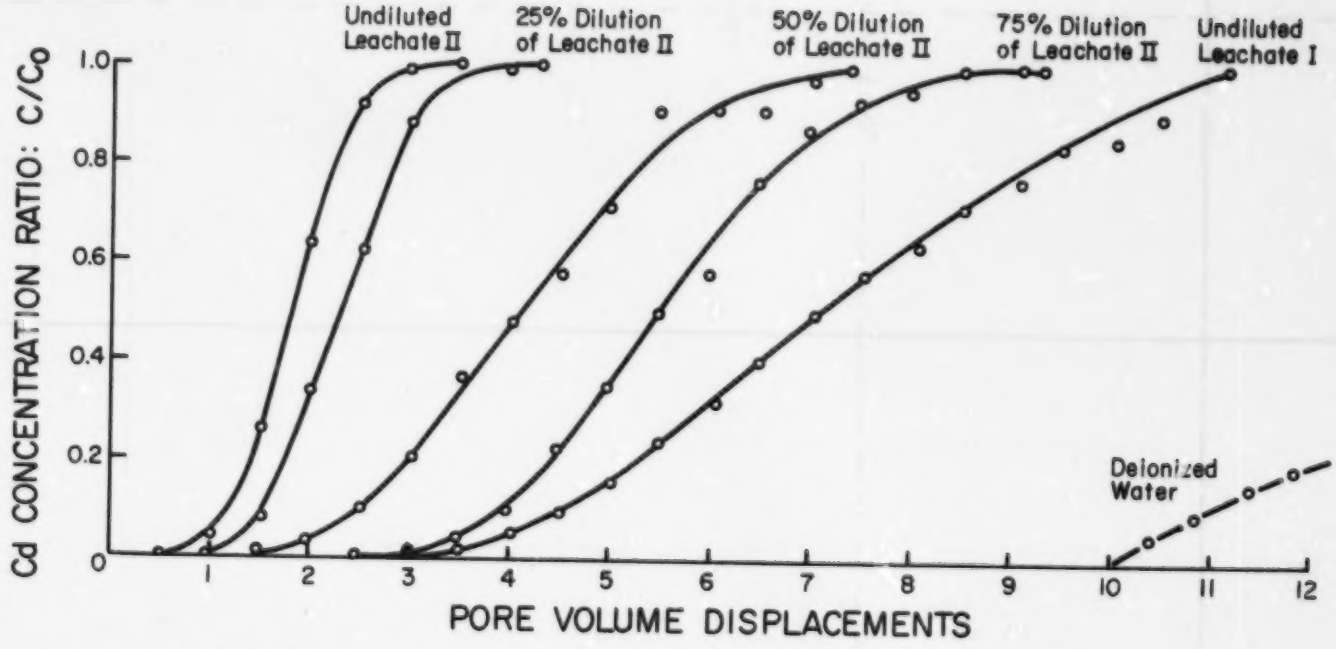

Figure 5. Effect of aqueous dilution on Cd concentrations in soil column effluents moving through Ava sicl at a flux of 8 cm/day.

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constituents.

The question that is posed by this finding is what leachate characteristics exert a real influence on migration rate? Three characteristics seem to stand out as varying widely among the leachates: (a) Organic substances, as evaluated by TOC; (b) total dissolved solids or inorganic salts, as evaluated by electrical conductivity (EC) or combustion to determine inorganic salts; and (c) pH, as evaluated by H^+ activity. All of these parameters lend themselves to ready and reproducible measurement. Lower levels of TOC and EC and higher pH values favored retention of Cd by the Ava sicl. However, further research is needed before these leachate characteristics can be evaluated in terms of quantitative influence on element migration through soils or on a practical basis for management planning in a disposal program.

Since pH changes often accompanied variations in MSW leachate characteristics, a study was undertaken to evaluate concentration changes in constituents at different pH levels for contact intervals of 5 and 72 hr, and leachate dilutions of 1:0, 1:1, and 3:1. Data reported in Table 10 show Cr solubility to be definitely pH dependent. When the pH was lowered from its natural value of 5.4 to 2.0 by addition of HCl, more and more Cr remained in solution. Cr solubility appeared to be influenced by time of contact with the leachate as may be seen by comparing the 5-hr with the 72-hr contact period in adjacent columns (Table 10). The trends of Fe concentration in solution for the same pH changes and times of contact followed those of Cr. The organic carbon content (TOC), on the other hand, was little changed in concentration by pH alteration from 5 to 2 nor did it appear to vary appreciably with standing from 0 to 72 hr, Table 11. Concentrations, however, were lower at 75% dilution than undiluted and 50% diluted solutions.

The electrical conductivity was much higher in the original solution than in the 50 and 75% diluted solution. The relatively small difference in EC between the 50 and 75% dilution is difficult to understand in view of the (a) slight differences in TOC between the undiluted and 50% diluted leachate and (b) wide differences between the 50 and 75% diluted leachate. The presence of an abundance of volatile organic acids and their salts could well account for this apparent buffering of ionization.

In a companion study to Cd, the effects of dilution with water and influence of pH on Cr solubility is dramatically illustrated in Figure 6. The soluble CrVI enriched in natural Leachate II declined rapidly with an increase in pH. Unlike Cd, however, Cr appeared to be more soluble in diluted than undiluted leachate.

Chromium solubility also was investigated in an experiment combining factors of (a) aqueous dilution and (b) bubbling with CO_2 since pilot studies indicated long time exposure of MSW leachate to CO_2 and excessive bubbling or aeration with CO_2 encouraged carbonate formation. The solubility of metals in the leachates could be influenced by carbonate precipitation resulting from the CO_2 treatment. The Cr enriched in Leachate II at pH 5.4 as CrVI disappeared from solution until the dilution reached about 95%. The pH had dropped slightly, however, from 5.4 to 4.9, Table 11. MSW leachates also are abundantly supplied with electron donors such as Fe and organic molecules

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TABLE 10. EFFECTS OF pH, CONTACT TIME, AND AQUEOUS DILUTION ON CONCENTRATION OF Cr, Fe, TOC, AND EC IN LEACHATE II

pH	Cr*		Fe		TOC		EC	
	5 hr	72 hr†	5 hr	72 hr†	5 hr	72 hr†	5 hr	72 hr†
	ppm		ppm		%		mmhos/cm	
	Undiluted Leachate II							
5.4	1	1	900	900	0.50	0.50	20	20
5.0	15	5	320	240	0.42	0.50	20	20
4.5	15	5	360	400	0.44	0.52	20	20
4.0	19	12	400	480	0.35	0.40	20	20
3.5	38	26	350	650	0.35	0.36	20	20
3.0	60	60	650	750	0.37	0.37	20	20
2.5	100	94	700	800	0.46	0.36	20	20
2.0	100	106	800	800	0.41	0.34	20	20
	50% Dilution							
5.0	14	20	205	208	0.43	0.46	7	6
4.5	23	22	233	233	0.41	0.47	7	8
4.0	53	40	295	275	0.43	0.43	8	9
3.5	82	88	355	350	0.42	0.43	9	11
3.0	83	100	415	388	0.43	0.40	9	11
2.5	98	108	450	422	0.39	0.36	11	12
2.0	100	115	470	460	0.43	0.41	12	15
	75% Dilution							
5.0	47	25	45	28	0.060	0.059	4	4
4.5	75	45	85	60	0.060	0.063	5	5
4.0	94	85	140	120	0.058	0.064	5	6
3.5	100	95	185	163	0.067	0.066	6	6
3.0	100	102	200	180	0.067	0.064	6	7
2.5	100	105	218	205	0.076	0.065	8	8
2.0	100	102	230	230	0.070	0.078	10	11

* Enriched in leachate at 100 ppm.

† Contact times for the undiluted Leachate II are 5 and 24 hr, not 5 and 72 hr as for the other leachates.

(From Fuller et al., 1979a)

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TABLE 11. EFFECT OF DILUTION OF MSW LEACHATE II WITH WATER ON THE SOLUBILITY OF Cr AND Fe, AND TOC, pH, AND EC

Leachate Concentration (%)	Original Leachate (pH)	Concentration after 72 hr bubbling with CO_2 pH	Cr(VI)*	Total Cr	Fe	TOC	EC
			(mg/l)				(mmhos/cm)
100	5.40	5.40	0.05	0.05	750	7,619	9,200
50	5.40	5.20	0.05	10	380	3,150	3,800
40	5.20	5.20	0.7	19	302	2,565	3,150
35	5.15	5.15	13	28	260	2,217	2,800
30	5.15	5.18	28	32	220	1,989	2,350
25	5.15	5.10	40	43	188	1,737	2,300
(25)†	(5.15)	(2.51)	(112)	(112)	(230)	(3,000)	(7,700)
(25)‡	(5.15)	(4.00)	(50)	(105)	(51)	(1,800)	(3,200)
(25)∫	(5.15)	(4.00)	(56)	(91)	(123)	(1,800)	(3,200)
20	5.03	5.03	53	55	148	1,381	1,800
10	4.95	4.90	76	77	80	720	1,040
5	4.90	4.71	90	92	37	325	590
2	4.50	4.40	98	99	15	140	200

* Cr was enriched in the leachate after diluting with water.

† The levels of pH, Fe, TOC, and the EC represent dilution effect in the presence of enriched Cr and pH adjustment to 2.51.

‡ The levels of pH, Fe, TOC, and the EC represent dilution effect in the presence of enriched Cr and pH adjustment to 4.00: Limestone Cr(VI) vs Cr(III) interaction studies.

∫ The levels of pH, Fe, TOC, and the EC represent dilution effect in the presence of enriched Cr and pH adjustment to 4.00.

(From Artiola and Fuller, 1979)

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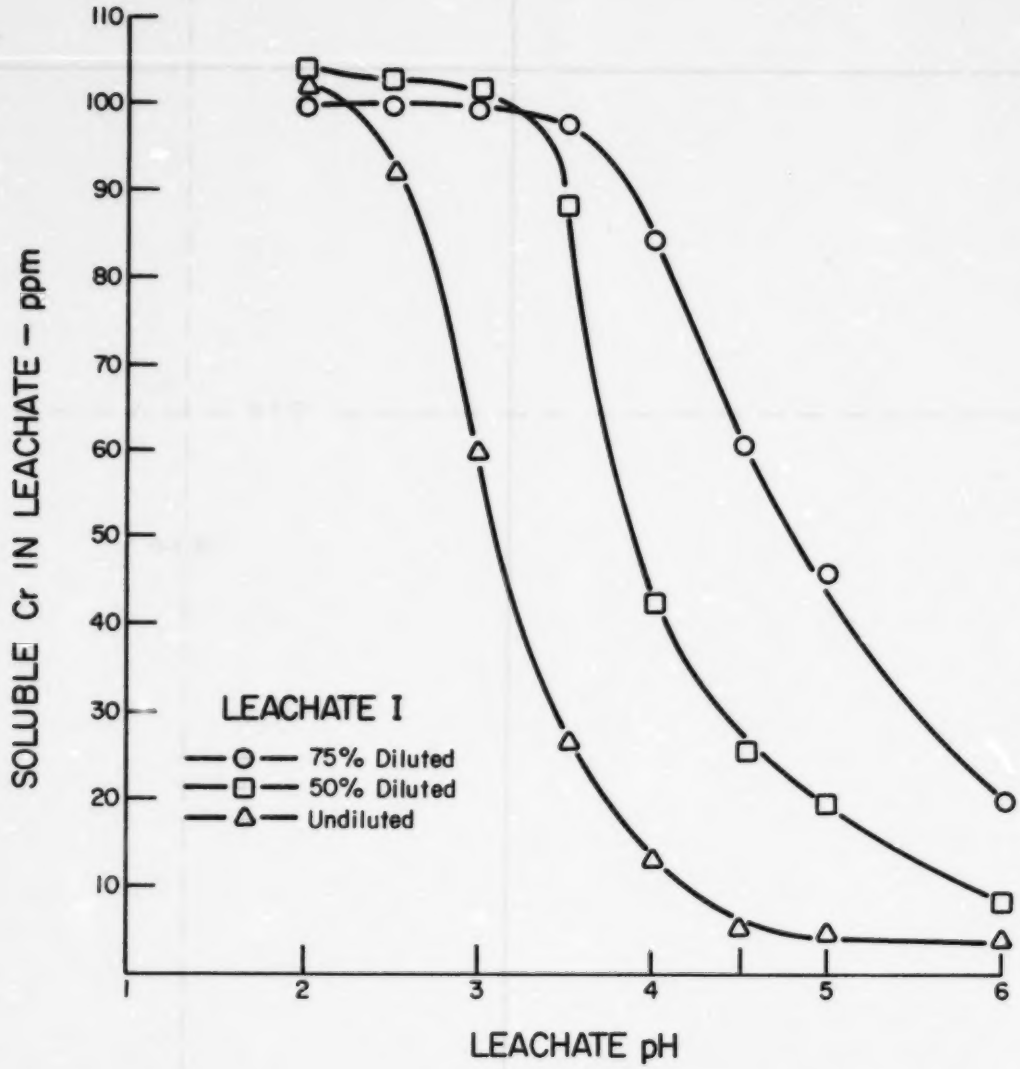

Figure 6. Influence of aqueous dilution and pH on the solubility of CrVI enriched into Leachate I at 100 ppm after stabilization of 48 hrs.

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that are capable of converting CrVI to the less soluble CrIII. Enriching leachate II with CrVI at 100 ppm resulted in approximately 18% reduction in soluble organic carbon (TOC). Iron precipitated also upon dilution since rust-colored hydroxide or hydrous oxide appeared although the amounts were not unusually high. The effect of dilution was reflected in lower TOC and EC measurements as the leachate was subjected to added increments of water, Table 11.

Effects of Organic Carbon (TOC) and Salts

The value of soils as landfill liner material will depend on their behavior when in contact with MSW leachates. In addition to the leachate variables already discussed, the total organic carbon (TOC), soluble Fe, and inorganic salts have been found to relate to the rate of trace metal movement from landfills (Fuller, 1977a, b). Further data demonstrating the interrelationships among these variables were accumulated, some of which are reported for Fe and Cd in Figures 7 and 8, respectively, and for Ni and Zn in Tables 12 and 13, respectively. Similar data for other MSW leachates and other soils have been published recently (Fuller et al., 1980; and Fuller et al., 1979a, b). In brief, it was found that the higher the soluble TOC, inorganic salts, and Fe, the higher the migration rates of Fe and Cd as illustrated in Figures 7 and 8. The differences between attenuation of these metals and concentrations of TOC, salt, and Fe are highly significant. Soil liners, whether dominated by sand, silt, or clay, therefore, will be much more effective for more dilute than for concentrated leachate. What the reason is for iron effects is not clear. Iron salts provide a good system for electron transfer just as with the organic carbon constituents, although it is recognized that the correlation may also be no more than coincidence. The effects of organic constituents and soluble salt concentration is easier to understand.

The behavior of Ni and Zn in soils was responsive to changes in concentrations of TOC and soluble inorganic salt (Tables 12 and 13) as was Fe and Cd. Effects of soluble leachate Fe on Ni and Zn migration rates were not studied independently since they appeared to be closely related to those of other inorganic soluble salts. Leachate iron, therefore, was included with the inorganic salt factor. Data in Table 12, for Ni, indicate that attenuation per unit weight of soil ranged for 3 to 4-fold greater at the lowest levels of TOC (2,000 ppm) than the highest (7,000 ppm). For Zn the differences were even greater ranging from 7 to 14-fold. In the Zn study the TOC levels compared well with those of Ni but the salt levels varied from a high of 2,600 ppm to a low of roughly 200 ppm (Table 13).

Effect of Specific Ion Concentration

The interaction between different concentrations of a specific element in solution and soil has long been a matter for speculation. Most of this speculation has been related to soil cation and/or anion exchange capacity. A common belief among those inexperienced in soil science is that soils possess a certain capacity to retain a specific metal ion (e.g. Cd, Ni, Zn, etc.), and that when this certain capacity is satisfied, the specific metal ion is free to migrate. In a sense, this is true. Yet when low levels

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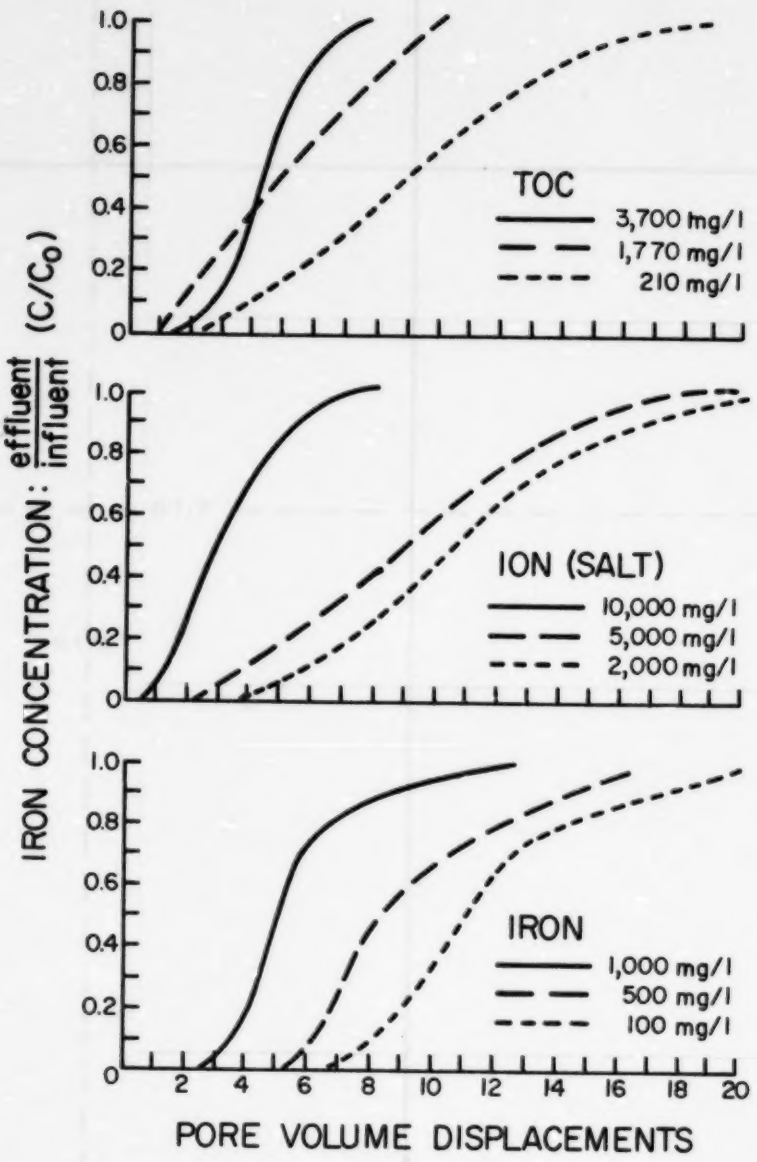

Figure 7. Effect of total organic carbon constituents, salt, and iron on the migration rate of Fe from Leachate II through Kalkaska sand.

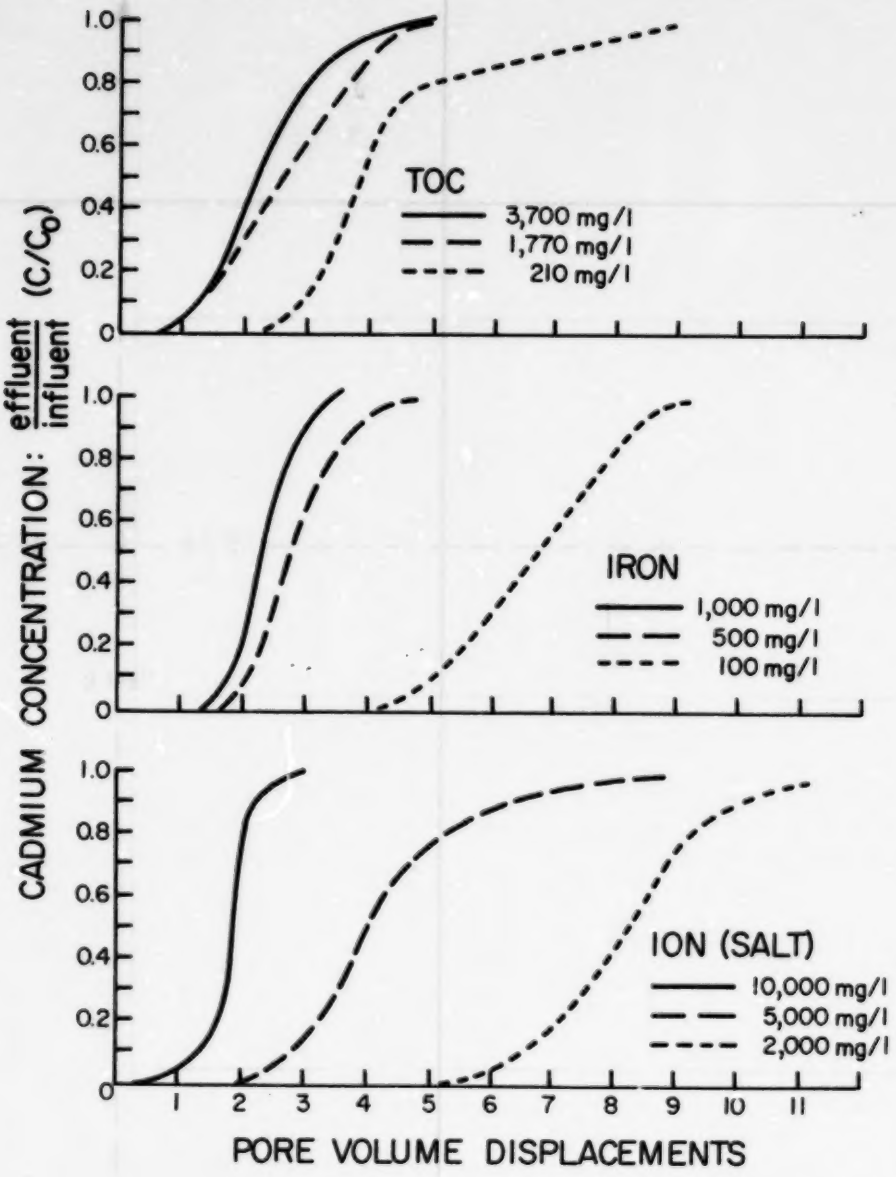

Figure 8. Effect of total organic carbon constituents, salt, and iron on the migration rate of Cd from Leachate II through Ava silty clay loam.

TABLE 12. EFFECTS OF DIFFERENT CONCENTRATIONS OF ORGANIC CARBON AND SOLUBLE INORGANIC SALT IN MSW LEACHATE II ON THE Ni RETAINED BY SIX SOILS

Leachate Constituent		Ni Retained per Weight of Soil					
TOC	Inorganic Salt	Davidson clay	Chalmers silty clay loam	Ava silty clay loam	Anthony sandy loam	Kalkaska sand	Wagram sand
--- mg/l ---		mg Ni/g soil					
1,950	2,010	0.26	0.40	0.33	0.22	0.14	0.04
2,100	940	0.30	0.57	0.50	0.20	0.18	0.07
1,190	2,090	0.20	0.55	0.19	0.20	0.13	0.04
1,280	990	0.34	0.78	0.43	0.30	0.26	0.05
1,140	600	0.36	0.87	0.48	0.26	0.26	0.09
590	2,350	0.18	0.63	0.34	0.24	0.20	0.04
550	800	0.29	1.00	0.60	0.25	0.22	0.03
530	400	0.64	1.37	0.75	0.80	0.40	0.05

TABLE 13. EFFECTS OF DIFFERENT CONCENTRATIONS OF ORGANIC CARBON AND SOLUBLE INORGANIC SALT IN MSW LEACHATE ON Zn RETAINED BY SEVEN SOILS

Leachate Constituent		Zn Retained per Weight of Soil						
TOC	Inorganic Salt	Davidson clay	Nicholson silty clay	Fanno clay	Ava silty clay	Anthony sandy loam	Kalkaska sand	Wagram sand
---- mg/l ----		mg Zn/g soil						
2,620	2,000	0.30	0.40	0.51	0.32	0.17	0.16	0.07
2,500	1,000	0.40	0.44	0.91	0.49	0.34	0.31	0.10
1,400	2,000	0.70	0.96	nd*	0.55	0.35	0.32	0.11
1,370	1,000	0.96	1.08	nd	0.65	0.51	0.34	0.12
1,070	500	1.51	1.54	1.25	1.57	0.70	0.52	0.52
170	2,000	0.99	nd	2.72	1.66	0.60	0.37	0.07
190	1,000	1.34	nd	2.83	2.23	0.92	0.40	0.18
210	500	4.70	nd	3.74	4.40	1.86	2.03	0.75

* Not determined; no values available.

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(i.e., ppm or ppb) of a metal ion occur, for example, in a municipal solid waste landfill leachate along with varied high levels of other soluble salts (ions), there is no real fixed (threshold) value beyond which the metal will or will not migrate. The concentration of the metal ion in solution determines the amount retained by the soil. This is best illustrated by data presented later.

SOLUTION FLUX AFFECTING METAL MOVEMENT FROM LANDFILLS

Early in the research program, we found that certain metals in MSW landfill leachate, such as Fe and Al, migrated at a slower rate through soil when the solution flow (flux) was the slowest (Table 14). Korte et al. (1976b) found that of several metals added to leachate (Be, Cd, Cu, Cr, Fe, Hg, Ni, Pb, Zn), Cr was the most susceptible to changes in leachate flow rate (flux). As a consequence of these observations we examined the effect of three fluxes on leachate containing 60 ppm Cr and passed through Kalkaska sand and Fanno c (Figure 9). Data for Figures 9 and 10 were obtained with the use of a constant flow pump and a fraction collector.) The most evident manifestation of flux is a comparison of the point at which initial detection took place. Chromium appeared in the Kalkaska s effluent before the displacement of 3 pvd with both of the faster rates, (Figure 9). With the slower rate, it was not until 10 pvd that Cr was detected in the effluent. Chromium reacted similarly to flux in experiments with Fanno c.

The results for Cd in the same soil (Figure 10) were less dramatic. The initial detection of Cd was delayed for the slower rates, but the overall differences are rather small. This type of research may yield valuable information about disposal site selection and water management of landfill. Liner management by control of soil compaction or clay content of liner material to establish the most effective flux for metal retention is suggested. Flux measurements may also lead to additional information on identifying reaction rates and elucidating mechanisms of attenuation.

A research program was therefore developed to evaluate further the importance of leachate flux on the attenuation of several potentially hazardous pollutant metals (As, Be, Cd, Cr, Fe, Ni, Se, V, and Zn). In addition to flux and type of metal, two other variables were included -- soil and concentration of metal in the leachate. Leachate II contained such high levels of salts, Fe, and TOC that it required dilution to maintain stable levels of certain heavy metals in solution. Chemical characteristics of these leachates (water diluted and natural) appear earlier in Table 11. Both Leachates I and II were used for Cd studies, whereas Leachate I was used for Cr since it precipitated readily and almost completely in Leachate II. Leachate II and III was used for the As, Be, Cd, Fe, Ni, Se, V, and Zn studies.

Flux and Leachate Variables

The influence of flux on Cd retention in two municipal solid waste landfill leachates is shown in Table 15. Differences in soil retention of Cd as a result of flux of Leachate I (which was lower in concentration of constituents than Leachate II) are very modest, despite the threefold difference in flux. This confirms the lack of clear-cut differences produced by

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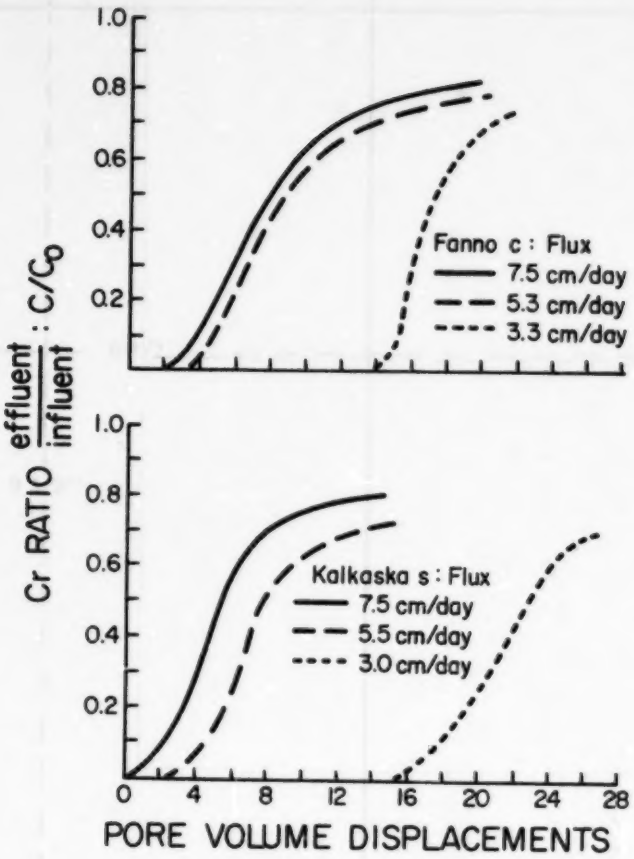

Figure 9. Migration rates of Cr in MSW landfill Leachate I in Kalkaska s and Fanno c as related to three solution flow rates (flux).

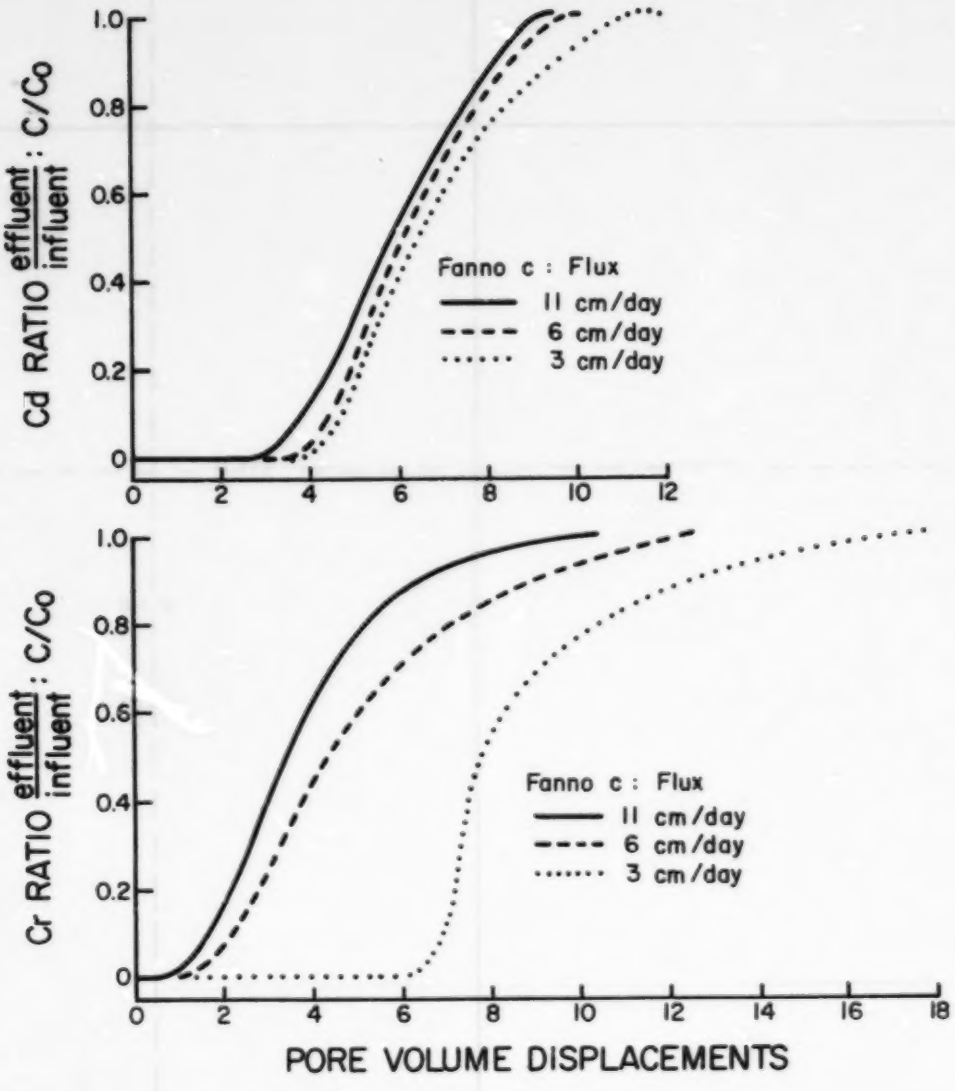

Figure 10. Migration rates of Cd and Cr in MSW landfill Leachate I through Fanno c as related to three flow rates.

TABLE 14. COMPARISON OF Fe AND Al ATTENUATION AT TWO SOLUTION FLOW RATES THROUGH NICHOLSON sic*

pvd	Soil column A†			Soil column B†		
	Time of contact (days)	Concentration in effluent		Time of contact (days)	Concentration in effluent	
		Fe	Al		Fe	Al
		(-mg/liter--)			(-mg/liter--)	
0.5	1	0.2	0	1	0.2	0
1.0	2	0.2	0	4	0.4	0
1.5	3	0.3	0	6	0.5	0
2.0	4	12	0	12	2.6	0
2.5	5	104	2	16	1.6	0
2.0	6	136	3	21	0.3	0
3.5	7	230	8	29	0.7	0
4.0	8	300	10	33	2.2	0
4.5	9	340	16	37	1.8	0
5.0	10	500	44	46	1.6	0
5.5	11	780	125	55	1.1	0
6.0	12	830	140	60	2.0	0
6.5	13	830	160	65	110	1.0

* Soil columns were 10 by 22-cm PVC cylinders
† Column A was packed to a bulk density of 1.53 and column B to 1.75. (from Alesii et al., 1980)

TABLE 15. INFLUENCE OF FLUX ON THE RETENTION OF Cd FROM MSW LANDFILL LEACHATE I BY THREE SOILS

	C/C_o								
	Kalkaska s			Ava si cl			Davidson C		
pvd No.	3.5 cm/day flux†	7.0 cm/day flux	10 cm/day flux	3.5 cm/day flux	7.0 cm/day flux	10 cm/day flux	3.0 cm/day flux	6.5 cm/day flux	10 cm/day flux
0-1	0	0	0	0	0	0	0	0	0
1.5	0	0.02	0.05	0.01	0.01	0.05	0	0	0
2.0	0	0.03	0.13	0.03	0.03	0.17	0	0	0
2.5	0.04	0.05	0.22	0.10	0.10	0.34	0	0	0
3.0	0.17	0.20	0.34	0.20	0.21	0.50	0	0	0
3.5	0.30	0.35	0.51	0.37	0.34	0.62	0	0	0.04
4.0	0.42	0.38	0.58	0.48	0.45	0.71	0.01	0.01	0.10
4.5	0.60	0.47	0.74	0.58	0.57	0.74	0.07	0.08	0.22
5.0	0.65	0.57	0.77	0.71	0.64	0.76	0.18	0.14	0.30
5.5	0.68	0.63	0.83	0.74	0.73	0.92	0.29	0.36	0.41
6.0	0.74	0.79	0.84	0.81	0.80	0.96	0.37	0.46	0.59
6.5	0.74	0.83	0.84	0.90	0.84	0.97	0.50	0.59	0.59
7.0	0.76	0.84		0.91	0.90	1.00	0.66	0.71	0.72
7.5	0.76	0.84		0.91	0.95		0.67	0.78	0.78
8.0	0.76	0.84		0.91	0.96		0.74	0.84	0.84
8.5				0.93	1.00		0.76	0.93	0.92
9.0				0.97			0.78	0.98	0.98
9.2				1.00			0.82	0.98	0.98
9.5							0.92	0.99	1.00
10.0							0.99	1.00	
10.5							1.00		

† Flux (flow velocity) is expressed as discharge (cm^3) per unit area (cm^2) per day: cm/day will relate as rainfall.

flux variations reported earlier with Cd in the same leachate (Figure 10). Figure 11 where Cd is present in Leachate II, also fails to indicate any dramatic influence of flux on Cd migration in the six different soils, even though retention differences between soils is significant. The same appears to be true for Cd in natural Leachate II, where flux was varied widely from 1 to 15 ml/ha (Figure 12). By calculating data in Table 16 on the basis of Cd retained per given weight of soil per given volume of full strength Leachate II, however, flux was revealed to have a significant (0.01 level, F = 96) influence on Cd attenuation that did not appear to occur with the lower concentration, higher pH (6.4) Leachate I or diluted Leachate II. Data included in all of the flux research represent metal retention values at breakthrough (i.e. when concentration of the metal in the effluent = influent as indicated by $C/C_0 = 1.0$).

Flux and Soil Variables

Retention of Be, Cd, Cr, Ni, and Zn in all of the soils appeared to be significantly responsive to variations (two- to three-fold differences) in flux according to data compiled in Table 17. More metal remained in those soils when applied at a lower flux than at a higher one. Clay soils also retained more of the test metal than sandy soils but the relative differences in retention of a given metal in the different soils due to flux was similar. Soil texture or clay content appears to be a far greater factor in metal attenuation than flux.

Flux and Metal Types

The interaction of flux with retention of Cd, Ni, and Zn in different soils is shown in Table 17 and Figures 11, 12, 13, and 14. Metal retention by soils to breakthrough ($C/C_0 = 1$) is very similar for the three elements. A case may be made for Cd being slightly more mobile than Ni or Zn, but the differences for the same soil do not exceed 3 or 4 pvd. The shape and position of the different flux curves are nearly identical for a given soil. Differences in flux for the three metals appear to be so small as to be of little practical significance, judging from Figure 11, 12, 13, and 14. Accumulative retention data for the various metals in different soils (Table 16) also reveal few significant differences in the interactions of various kinds of metals and flux.

On the other hand, Be and Cr are more sensitive to changes in flux (Table 16 and Figure 15) compared with Cd, Ni, and Zn (Figures 11, 13, and 14). Between 12 and 42% more Be remained in the soil when flux was slowed about three-fold. In the more dilute Leachate I, Be reacts more like the group of metals represented by Cd, Ni, and Zn than the metallic Cr anion. Beryllium thus seems to be between the two groups with regard to flux sensitivity, perhaps in a class of its own. Nevertheless, Be responds to changes in flux, and its attentuation in leachate possibly may be managed favorably and practically through flux manipulation by slowing solution traverse through soil.

Chromium retention by five soils (Table 16) reacted clearly to flux change of Leachate I. These results agree with responses illustrated earlier

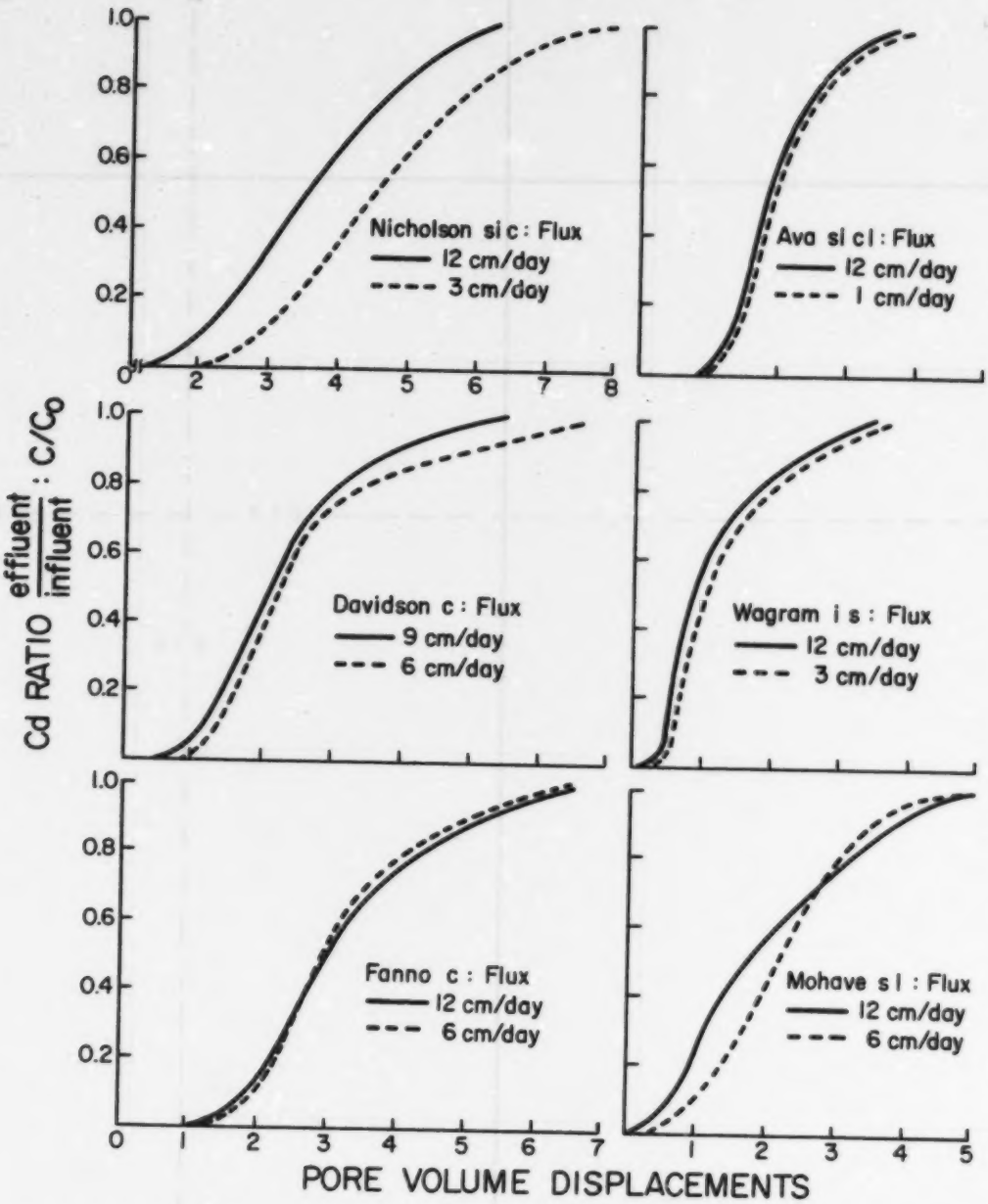

Figure 11. Migration rate of Cd in MSW landfill Leachate II in six soils as related to two solution flow rates (flux).

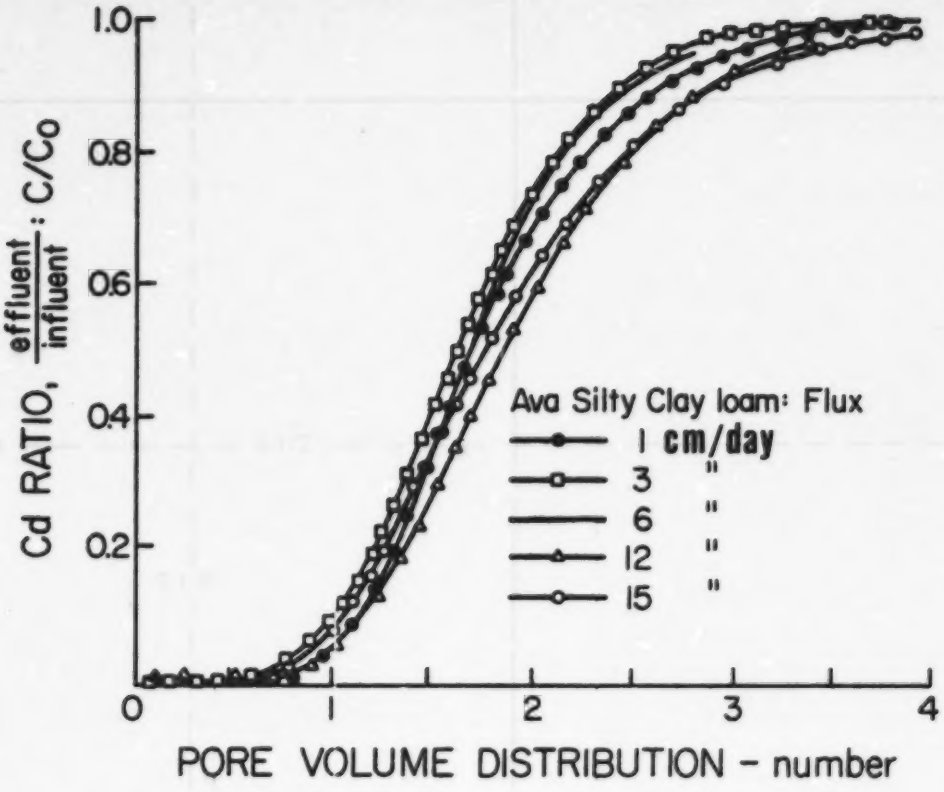

Figure 12. Influence of widely varying fluxes of MSW landfill Leachate II on Cd retention by Ava si c l. +Flux (flow velocity is expressed as discharge (cm^3) per unit area (cm^2) per day (cm/day will relate as measured rainfall).

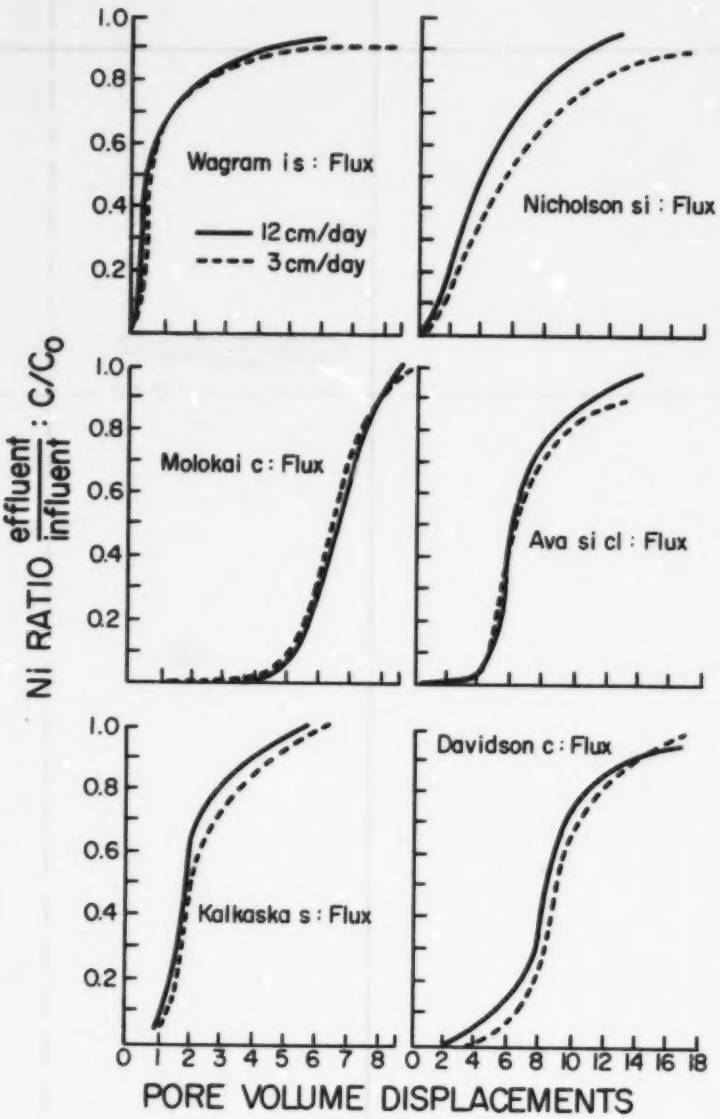

Figure 13. Nickel attenuation in six soils as influenced by different flow rates (flux) of MSW landfill Leachate II.

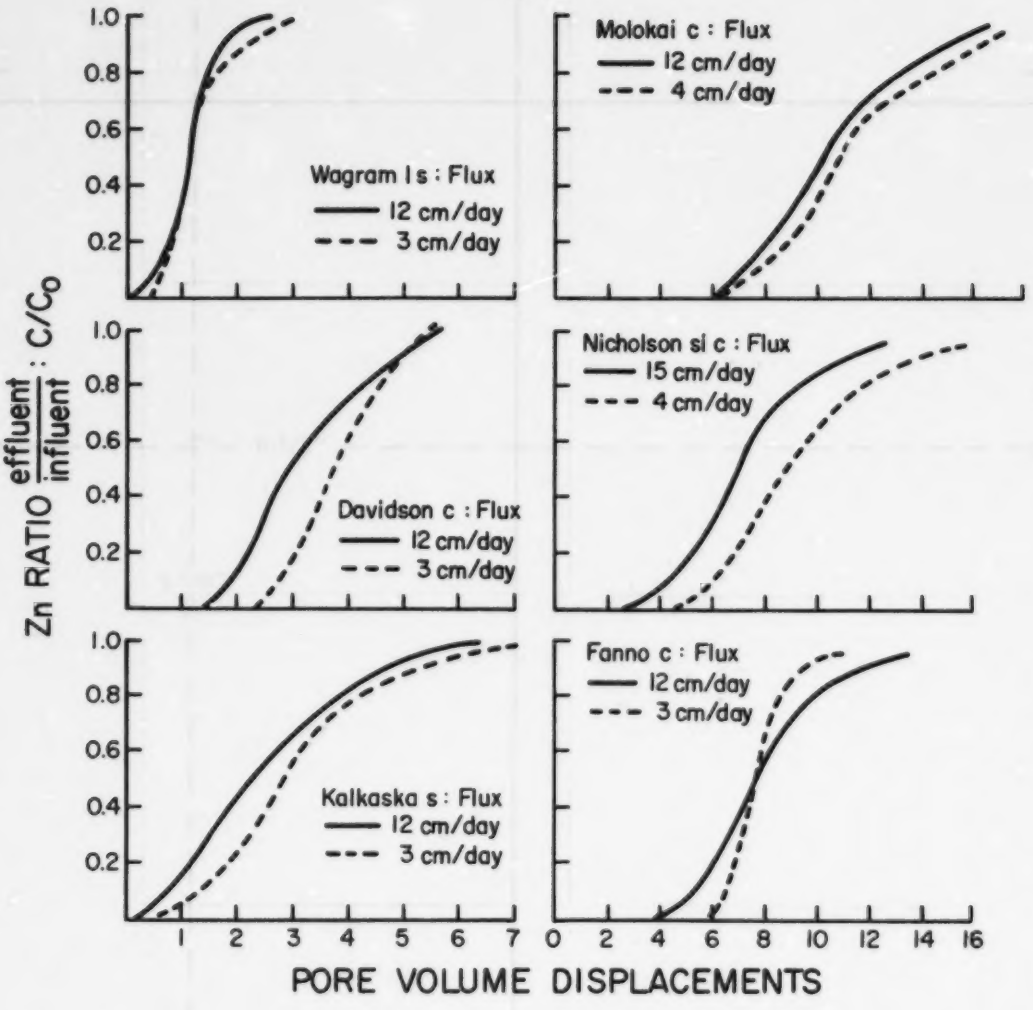

Figure 14. Zinc attenuation in six soils as influenced by different flow rates (flux) of MSW landfill Leachate II.

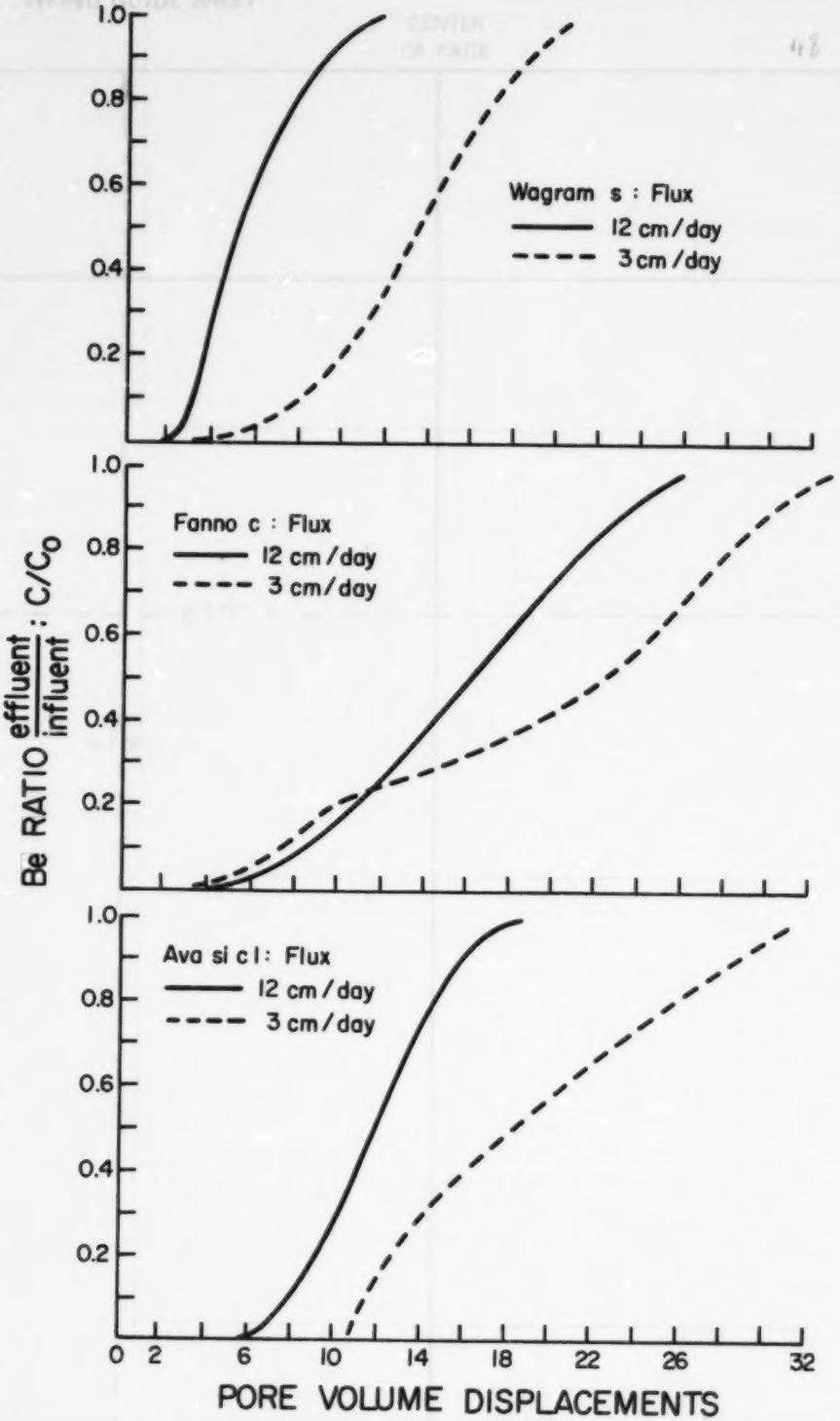

Figure 15. Beryllium attenuation in three soils as influenced by different flow rates (flux) of MSW landfill Leachate II.

TABLE 16. EFFECT OF FLUX ON THE RETENTION OF SELECTED METALS IN MSW LANDFILL LEACHATE II PASSED THROUGH NINE SOILS.

Soil Type	Flux Range (cm/day)	Metal Retained by Soil: Cd (µg of metal retained per g soil per liter leachate)‡	CrVI+	Ni	Zn	Be
Davidson clay	3.0- 6.6	151	194	181	226	1,491
	6.7-10.7	130	61	175	208	810
	13.7-16.7	119	nd§	139	182	703
Molokai clay	3.4- 7.3	254	nd	269	255	2,462
	9.2-10.2	220	nd	279	184	2,198
	14.2-18.0	219	nd	276	175	1,915
Nicholson Silty clay	3.0- 4.8	186	276	159	203	1,442
	7.0- 9.8	nd	109	nd	185	1,015
	14.2-17.1	120	57	143	179	629
Fanno clay	3.3- 4.3	224	171	225	215	690
	6.8- 8.3	nd	100	223	213	565
	12.7-16.1	171	58	188	175	463
Mohave (CO_2) clay loam	3.4- 6.2	115	60	nd	nd	nd
	7.3	nd	56	nd	nd	nd
	14.2-19.0	92	49	nd	nd	nd
Ava silty clay loam	1.2- 4.6	261	nd	209	192	743
	7.3	255	nd	nd	165	nd
	13.2-15.0	134	nd	169	151	578
Anthony sandy loam	3.4- 4.1	133	nd	153	114	666
	7.3- 8.3	121	nd	137	105	nd
	11.5-16.8	116	nd	123	89	359
Kalkaska sand	2.4- 4.4	159	188	141	115	466
	6.5- 7.1	148	135	120	106	368
	13.8-16.5	144	112	118	102	209
Wagram sand	3.6- 5.5	83	nd	75	100	472
	7.3	80	nd	nd	107	nd
	14.3-14.5	72	nd	65	106	99

+ Cr precipitates out of solution above pH 4.0 when in MSW landfill Leachate II. Cr was evaluated on Leachate I acidified to pH 4.0.

‡ µg/g per l means µg of metal retained per g of soil per liter of MSW landfill leachate passed through the 5- by 10-cm soil column. To convert µg/g per cm depth of leachate such as relates to rainfall measurements, multiply by 0.019635. To convert µg/g per cm (to pore volume of effluent from column)multiply the above column of figures by 10 cm and divide by porosity.

§ nd means not determined.

in Figure 9. Statistically, the µg of Cr retained per g of soil per ml of MSW Leachate I is significantly correlated (0.05) with flux. The slower the rate of leachate flow through the soils, the greater the tendency for Cr retention.

Flux and Metal Concentration

The effect of this interaction between leachate flux and Cd concentration in MSW landfill Leachate II on Cd retention by Ava silty clay loam was not found to be significantly different for three flow rates (Table 17). However, Cd retained by the soil in terms of amount per weight of soil per volume of leachate is significantly related to and proportional to the concentration of Cd in the influent. For Cd concentrations of 5.5, 11, and 100 the µg Cd retained of soil per ml of leachate averaged 0.0072, 0,0157, and 0.1502, respectively. Thus, the retention is directly proportional to the influent Cd concentration. Concentration of potential pollutants such as Cd, Ni, and Zn in leachate influences the absolute amount of the element retained by soil more than any one single factor, except perhaps clay content of the soil.

CRUSHED LIMESTONE LINERS

The following discussion evaluated the influence of crushed agricultural limestone, placed in a layer over soil, on the migration rate of As, Be, Cd, Cr, Fe, Ni, Se, V, Zn, and TOC in MSW landfill leachates. Because of the marked difference in attenuation characteristics between the cation- and anion-forming metals (Fuller et al., 1979), the discussion of each is separated.

Any attempt to minimize the migration of constituents of solid waste landfill leachates (or any leachates) requires soil modification from its natural state to make it more homogeneous. The next step necessary is the installation of barrier material to delay migration further and help hold contaminants in place. Underground waters, which are being used more and more for food crop irrigation and direct domestic consumption, must be protected.

Cations - Be, Cd, Fe, Ni, and Zn

The use of crushed agricultural limestone as a soil liner significantly delays the migration of soluble Be, Cd, Fe, Ni, and Zn in MSW landfill Leachate II (Table 18). The difference between attenuation of the metals passed through limestone lined and unlined soils ranged between two and three-fold in any of the six soils reported. The effect of the limestone barrier on retention of the five metals contained in the MSW leachate, however, varied both with the kind of soil and kind of metal. A thicker layer of limestone (i.e. 2 cm) would have greatly accentuated the barrier properties of limestone but would have prohibited quantitative evaluations. For example, when 5 cm of limestone was used in preliminary experiments, the metals were retained so well, months went by with but little evidence of metal appearing to pass through the soil column into the effluent. A thinner layer (2 cm) had to be used because no data were being generated for comparative purposes.

TABLE 17. CADMIUM ATTENUATION AS INFLUENCED BY FLUX AND METAL CONCENTRACTION IN MSW LANDFILL LEACHATE II PASSED THROUGH AVA SILTY CLAY LOAM

Cd in Leachate II Influent	Soil Column FLUX[+]	Cd Retained at C/C_o = 1	
		Total Held by Soil in Column	Metal Attenuated per g of soil per cm Depth of Leachate Passed through Column[‡]
(mg/liter)	(cm/day)	(µg)	(µg/g per cm)
5.5	7.0	730	0.14
5.5	10.5	630	0.13
5.5	14.5	700	0.11
11.0	7.5	1,730	0.30
11.0	10.9	2,000	0.32
11.0	14.2	1,980	0.31
100.0	7.5	18,170	3.06
100.0	11.0	18,000	2.95
100.0	14.6	18,190	2.92

[+] Flux (vlow velocity) is expressed as discharge (cm^3) per unit area (cm^2) per day (cm/day will relate as measured rainfall).

[‡] To convert µg /g per cm (pore volume of effluent) multiply these figures by 10 cm and divide by porosity.

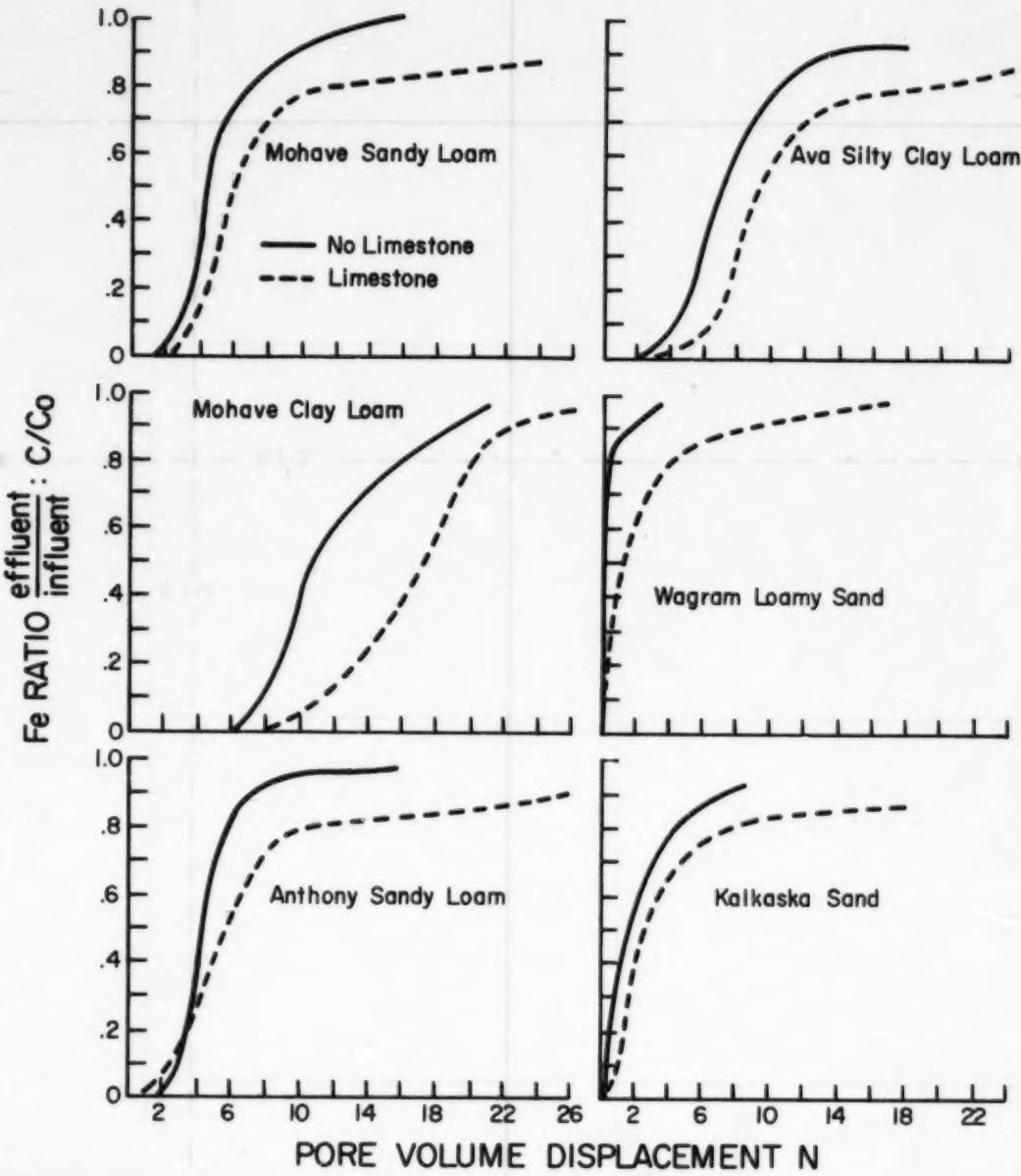

Figure 16. Effect of crushed limestone layered (2 cm) over six soils on the retention of Fe from MSW landfill Leachate II.

TABLE 18. RELATIVE EFFECT OF CRUSHED LIMESTONE LINER PLACED OVER SOIL ON THE RATE OF MIGRATION OF CATION-FORMING METALS IN MSW LANDFILL LEACHATE I

Metal	Pore Volume Displacement to Achieve the Same $C/C_o \approx 0.8$											
	With Limestone Layer with Soil						No Limestone Layer, Soil Only					
	Davidson c	Avasicl	Anthony sl	Mohave sl	Kalkaska s	Wagram s	Davidson c	Avasicl	Anthony sl	Mohave sl	Kalkaska s	Wagram s
Be	30	29	35	30	30	35	10	16	15	15	18	10
Cd	30	35	40	38	35	35	16	18	28	15	18	6
Fe	31	31	35	36	30	25	21	26	15	25	10	10
Ni	40	35	30	35	28	24	20	15	11	15	7	10
Zn	30	25	30	32	25	30	10	11	15	18	12	16

The data presented, therefore, are relative and yet serve a practical purpose for liner management. Effectiveness is directly related to and proportional to the thickness of the crushed limestone layer, providing channeling and piping through the barrier is at a minimum.

Differences in attenuation due to limestone between the different metals in Leachate I was not highly significant according to the data reported for the six soils in Table 18. However, in another more extensive study (Artiola and Fuller, 1980), attenuation effects of limestone barriers were found to be significantly higher for Be and significantly lower for Cd than the other metals.

The influence of limestone on the migration rate of the five metals through all soils was determined using MSW Leachate II. But because of space limitations and the similarity in basic results for all metals, only the data of one, Fe, is plotted in detail (Figure 16). The cumulative total Fe retained and number of pore volume displacements to achieve the same C/C_o is much greater in the lined than the unlined soil.

Statistically, the F value of 96.3 is significant at the 0.01 level for Fe retention due to limestone, according to data in Table 19. There also is a significant difference between the effectiveness of different soils for retaining natural MSW leachate Fe (Table 19). Those soils containing the most clay retained more Fe than the sandier soils, although the ratio of silt to sand had some influence on this outcome. For example, more than 90% of the leachate Fe was retained by Davidson and Molokai clays by the time C/C_o reached 0.8, whereas the Kalkaska and Wagram sands retained less than 36% of the Fe at the same C/C_o.

The total retention of Fe also correlates significantly with the clay content of the soils (Table 19). Davidson clay held more than five times as much leachate Fe/g of soil as the Kalkaska and Wagram sands. The nine-fold difference between Molokai clay and these sands is even more dramatic. Based on Fe retention per units of surface area, clay again appears to be a very effective attenuator compared with sand or silt. The relatively high values of Fe held per unit of surface area for the Kalkaska and Wagram sands make it seem that these sands have unusual surface activities. The data in these cases are misleading since landfill leachate collected under CO_2 and displaced through soil always will form some precipitation, even along the tubing approach in the soil column from the reservoir. Physical as opposed to chemical precipitation becomes more prominent at each successive leachate displacement through the sand columns. However, this is a small point in view of the great difference between <u>total</u> surface area per unit weight of sand and clay and the <u>total</u> retention associated with the surface.

After the concentration of Fe in the effluents from both lined and unlined soils stabilized at some level ranging between C/C_o of 0.8 and 1.0, deionized water was displaced through the columns at a pvd number equal to that used for landfill leachate earlier, to ascertain the retention stability of the limestone- and soil-attenuated Fe. The results (Table 20) show that solid waste leachate Fe is rather tightly held against leaching action of water both by the limestone and the soil. Only a small percentage of Fe (2

TABLE 19. RETENTION OF Fe FROM NATURAL MUNICIPAL LANDFILL LEACHATE II PASSED THROUGH 11 SOILS AS RELATED TO UNIT WEIGHT AND SURFACE AREA

Soil	Clay Content,(%)	Pvd Number*	Fe Attenuated†		
			Total Fe,(mg)	mg Fe/g Soil	µg Fe/m^2 Surface Area
Davidson c	52	25	922	2.597	51
Molokai c	52	20	1671	4.803	71
Nicholson sic	49	22	1462	4.097	34
Fanno c	46	22	1430	3.907	32
Mohave (Ca) cl	40	20	1061	2.962	21
Chalmers sicl	35	18	889	2.448	20
Ava sicl	31	16	680	1.874	30
Anthony sl	15	11	383	1.491	28
Mohave sl	11	16	470	1.090	28
Kalkaska s	5	11	222	0.445	50
Wagram s	4	10	210	0.410	51

*Pore volume displacements necessary to achieve breakthrough (i.e. $C/C_o = 1$), or at peak C/C_o, plateau between 0.8 and 1.0.

†mg Fe attenuated equals mg Fe added minus mg Fe in leachate effluent.

TABLE 20. EFFECT OF CRUSHED LIMESTONE LINER AND LEACHING WITH DEIONIZED WATER ON THE RETENTION OF SOLUBLE IRON FROM NATURAL LANDFILL LEACHATE PASSED THROUGH 11 SOILS

Soil	Pvd Number*	MSW Leachate Fe Retained in Soil Column (%) With Limestone Layer (2-cm) Before H_2O Leach†	With Limestone Layer (2-cm) After H_2O Leach†	Without Limestone Layer Before H_2O Leach	Without Limestone Layer After H_2O Leach
Davidson c	25	94	91	64	59
Molokai c	20	97	96	71	65
Nicholson sic	18	82	79	68	65
Fanno c	12	82	80	62	61
Mohave (Ca) c l	20	83	82	62	61
Chalmers sic	18	74	71	52	51
Ava sicl	16	70	68	44	40
Anthony sl	11	51	48	41	36
Mohave sl	16	44	41	34	31
Kalkaska s	15	36	33	20	13
Wagram s	17	34	31	15	12

*Pore volume refers to breakthrough where $C/C_o \simeq 1.0$ or at peak C/C_o plateau between 0.8 and 1.0.

†Soil columns were leached with deionized water by a pvd number equal to that used for landfill leachate, after effluent iron stabilized.

to 7%) appeared in the effluents of the many water displacements. Even after the lined and unlined columns of soil were leached with deionized water, there was still a highly significant difference in Fe retention favoring the limestone treatment. The F value of 87.8 is well within the 0.01 level.

Anions - As, CrVI, Se, and V

Anion-forming metals (As^{+3}, $CrVI^{+6}$, SE^{+4}, and V^{+5}) were enriched at 100 ppm levels into MSW landfill Leachate I and perfused through six soils with and without a limestone (2 cm) barrier to compare migration rates with the five cations just discussed. The data presented in Table 21 demonstrate that the migration rate of these metals (As, CrVI, Se, and V) is markedly slowed by crushed limestone. In fact, a comparison of data in Tables 18 and 21 reveals that the anion-forming metals were clearly less mobile than the cations in the presence of limestone. Moreover, the limestone effect appears to be more than additive (i.e. more than for soil alone plus limestone alone) as illustrated by Cr data in Table 22. This synergic effect occurred with all limestone-barrier soils and with all metals, enriched as well as natural. We do not have an explanation of the mechanisms involved at this time.

CRVI and CrIII react differently in soils. The CrIII migrates much more slowly than CrVI (Artiola and Fuller, 1979). CrVI readily reduced to CrIII when aerated at pH 4.0 with CO_2. Limestone appeared to encourage the CrIII formation by keeping the pH of the soil solution environment higher than that of the leachate. CrVI in a quartz sand-limestone column eluted first and reached an equilibrium after about 3 pore volume displacements, whereas CrIII progressively climbed to this level only after 10 pvd (Figure 17). The cation migrates much more slowly than the anion. Since the quartz sand has no appreciable retention qualities for Cr, the behavior of Cr is considered to be related to the limestone layer. The OH^- concentration of the bathing leachate solution was higher where a limestone barrier was involved (Artiola and Fuller, 1979). CrVI (as CrO_4^{2-}, $Cr_2O_7^{2-}$) is more mobile than CrIII at higher pH levels, however. Also, the CrVI anionic forms make them unsuitable for significant absorption by clay, since cation adsorption prevails greatly over anion adsorption in soil. Furthermore, limestone cannot be considered as particularly retentive of CrVI, per se. Despite these effects, however, limestone greatly slowed the migration of CrVI. It appears to do this by raising the pH. In addition, MSW leachates are abundantly supplied with organic carbon compounds and Fe^{2+} ions both of which readily donate electrons under the anaerobic conditions that prevailed. Thus the CrVI present in these leachates, had every opportunity to be reduced to CrIII fairly rapidly as indicated in Figure 17. The tendency for limestone to furnish OH^- to the leachates must be considered as an important factor in retention of the other anions of As^{+3}, Se^{+4}, and V^{+5}, also.

Organic Carbon

The soluble organic carbon compounds (TOC) in Leachate II had stabilized at about 7000 mg/l when the soil column and limestone barrier attentuation research was conducted. Neither the soil nor the 2 cm of crushed limestone barrier slowed the migration of TOC appreciably compared with that of the metals (Table 23). Some organic carbon compounds were retained during the

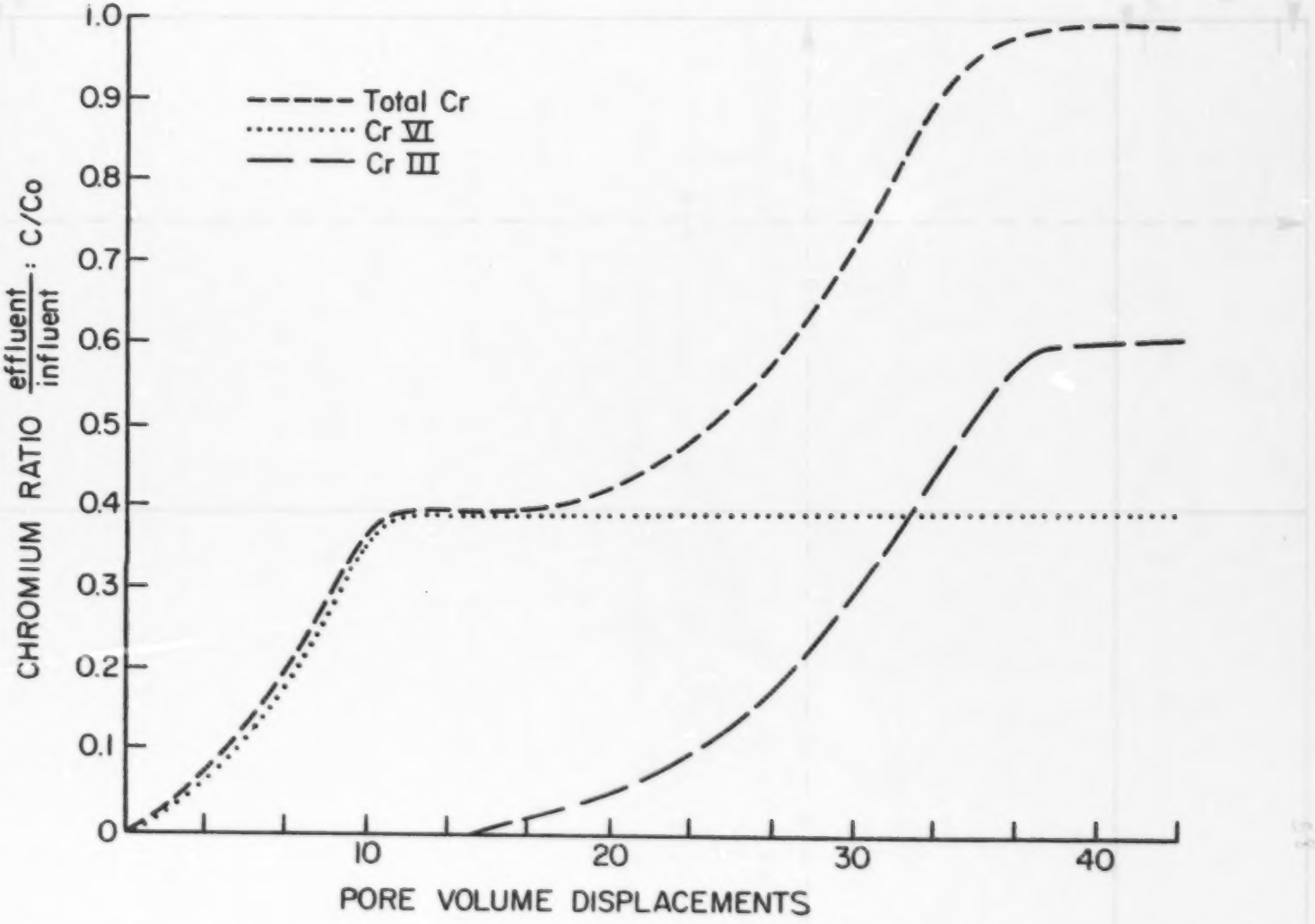

Figure 17. Relative migration rates of CrVI and CrIII enriched as CrVI into landfill Leachate II through 2 cm layer of crushed limestone over 10 cm coarse quartz sand.

TABLE 21. RELATIVE EFFECT OF CRUSHED LIMESTONE LINER PLACED OVER SOIL ON THE RATE OF MIGRATION OF ANION-FORMING METALS IN MSW LANDFILL LEACHATE I

Metal	Pore Volume Displacement to Achieve Breakthrough ($C/C_o \simeq 1$)											
	With Limestone Layer with Soil						No Limestone Layer, Soil Only					
	Davidson c	Ava sicl	Anthony sl	Mohave sl	Kalkaska s	Wagrams	Davidson c	Ava sicl	Anthony sl	Mohave sl	Kalkaska s	Wagrams
As (pH 5.2)	110	59	96	140	88	90	21	22	22	20	18	12
Cr (pH 2.5)	35	42	85	88	86	65	10	15	15	10	10	6
Cr (pH 4.0)	48	49	125	144	111	109	12	21	39	25	17	15
Se (pH 5.2)	125	68	130	142	92	85	22	35	19	21	19	17
V (pH 5.2)	51	55	70	92	82	69	20	25	16	15	17	10

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TABLE 22. EFFECT OF LIMESTONE ALONE AND LIMESTONE LAYERED OVER SOILS ON THE ATTENUATION OF Cr IN MSW LANDFILL LEACHATE II*

Soil			Ratio of Cr in Influent and Effluent	Pvd Number when Cr Concentration in effluent is at C/C_o given in Col. 4		
Series	Clay,%	pH	(C/C_o)	Limestone Alone	Soil Alone	Soil and Limestone
Davidson c	52	6.2	0.13	2	2	28
Ava sicl	31	4.5	0.38	5	21	49
Anthony sl	15	7.8	1.00	57	39	125
Mohave sl	11	7.3	0.76	46	25	144
Kalkaska s	5	4.7	1.00	57	17	111
Wagram s	4	4.2	1.00	57	15	109

* Leachate II had a pH value of 4.0, TOC of > 3000, and Fe of 300 ppm.

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TABLE 23. EFFECT OF CRUSHED LIMESTONE LINER ON THE RETENTION OF TOTAL ORGANIC CARBON FROM NATURAL MSW LANDFILL LEACHATE II PASSED THROUGH SOIL AND SAND

pvd No.	TOC* in Soil Column Effluent (ppm)					
	Davidson c	Molokai c	Nicholson si c	Fanno c	Mohave(Ca) sl	Chalmers si cl
1	4000	6400	6400	6800	6400	6500
2	5300	6300	5900	6800	6300	6600
3	6400	6700	6300	6600	6600	5700
4	6500	6600	6400	6500	6600	6000
5	6850	6500	6300	6600	6600	6200
6	6700	6600	6300	6700	6400	5800
7	6800	6200	6400	6600	6200	5600
8	6800	6200	6500	6500	6400	6100
10	6900	6100	6900	7000	6500	6200
12	7000	6800	6900	7100	6700	6300
14	7000	7000	6900	6900	7000	6300
16	7000	7100	6600	7000	6700	6600

pvd No.	Ava si cl	Anthony sl	Mohave sl	Kalkaska s	Wagram s	Quartz Sand
1	4600	6800	6600	6800	5550	6800
2	5100	6800	6400	6400	6000	6200
3	6000	6300	6500	6900	6900	6400
4	6800	6700	6600	6900	6300	6800
5	6750	7000	6800	6800	6600	6900
6	6700	7100	6800	6900	6700	7000
7	6700	6700	6700	6800	6800	7000
8	6800	6800	6400	6900	6800	7100
10	7000	6600	6500	7200	6800	6900
12	7200	6400	6600	7200	7300	6900
14	6900	7000	7000	7200	7600	6900

* Natural influent Leachate II contained ~ 7000 ppm TOC.

first 2-3 pvd. The nature of these is under study now. Limestone cannot be relied upon to be a particularly effective barrier to the downward migration of organic carbon compounds contained in MSW landfill leachates. In terms of actual quantity of constituent retained, however, the soil held far more TOC (< 0.45μ) than metal before breakthrough conditions were achieved. The influent leachates contained about 7000 ppm TOC compared to about 100 ppm metal. At such a high level of TOC the reaction sites of the soil presumably were quickly saturated.

Limestone Utilization

Limestone liners are not expected to remain as a permanent barrier since they are calcium carbonate ($CaCO_3$), a compound that reacts readily with acids and weak acidic solutions. MSW landfill leachates vary in acidity from pH values of about 4.0 when first generated to near neutral (Chain and DeWalle, 1976; Fuller and Alesii, 1980). Some older landfills support slightly alkaline leachates, but this is less common. Since the length of time limestone liners remain active in landfills determines their capacity for stabilizing metals, a balance sheet was maintained to accurately account for the Ca in the influent and effluent of the soil columns, while leachate displacement was going on. The Ca calculated as difference between column input and output minus soil-Ca was converted back to limestone $CaCO_3$. Data in Table 24 indicates limestone liners were utilized as a result of interaction with MSW leachates. The rate of loss was primarily a function of pH or acidity. Greater the acidity (lower the pH value) greater was the utilization or solubilization of the limestone. At pH levels within the range of most MSW landfill leachates, however, limestone dissolution was low (2 - 3.5%, Table 24). Data for the pH levels above 5.4 are not shown because they do not differ significantly from these values. Averages for the 6 soils at 20 pvd was 19.1, 8.4, and 1.8% for leachates at pH of 2.5, 4.0, and 5.4, respectively. The utilization of limestone alone in a 2 cm layer placed over pure quartz sand was similar to that over soils, Table 24. Also at pH 4.5 MSW Leachate II is shown (Fuller and Artiola, 1978) to be in between that solubilized at pH 4.0 and 5.4 above. There was no significant difference in utilization between the soils over which the limestone was placed; probably because no mixing took place. Limestone utilization was compared between three MSW landfill leachates having pH values of 6.4, 5.2, and 4.5 and between limestone layers of 2, 5, 10, and 15 cm. The results indicate again that greater utilization was associated with greater leachate acidity, Table 25. Also, utilization was roughly proportional to the thickness of the limestone layer.

Metal breakthrough ($C/C_0 = 1$) occurs in all instances before all the limestone is used. For example, at breakthrough for the cations Be, Cd, Fe, Ni, and Zn, the most limestone utilized was 4.2, 4.5, 2.9, 3.8, and 4.7% for the respective five metals. There is a real need to further study the efficiency of limestone utilization. Partial limestone utilization is reported by Pearson and McDonnel, 1975a, b in mine acid waste control and by DeVitt et al., 1976 in coal burning industries' air pollution control. The present belief is that the limestone particles become coated with reaction products such as gypsum and/or organics and other compounds in the reacting solutions. The surfaces are inactivated in this manner with encrusting substances blocking the possibility of solution contact being made with the bulk of the

TABLE 24. ABILITY OF MSW LANDFILL LEACHATE II TO SOLUBILIZE LIMESTONE PLACE OVER SOIL AND QUARTZ SAND ALONE

No.	Limestone (2 cm) Barrier Dissolved by Leachate II (%)						Quartz Sand
	Davidson c	Mohave sl	Ava si c	Anthony sl	Kalkaska s	Wagram s	
			Leachate pH Adjusted to 2.5*				
1	0.4	0.6	0.1	0.9	0.5	0.5	0.4
10	7.9	4.1	14.8	6.3	5.4	8.8	9.1
20	15.0	24.3	24.0	14.8	16.5	20.1	20.2
30	21.1	19.8	31.5	21.4	22.8	26.0	28.9
40	24.1	25.0	32.6	25.6	28.9	30.9	30.2
50	29.6	29.5	33.9	32.1	34.4	34.4	33.5
60	32.7	33.5	35.2	36.0	38.8	31.3	34.2
70	36.4	36.8	37.5	39.1	41.5	41.0	39.1
80	38.1	39.1	40.1	40.9	43.5	43.1	40.0
90	39.2	39.9	42.1	41.1	45.1	44.2	42.0
			Leachate pH Adjusted to 4.0*				
1	0.1	0	0.3	0.4	0.3	0.4	0.4
10	5.9	4.8	6.0	2.9	3.9	4.8	4.9
20	9.0	7.9	10.0	7.6	7.6	8.1	7.8
30	10.5	11.3	13.1	10.6	11.3	11.3	11.2
40	11.4	13.9	15.8	13.9	15.1	14.0	14.5
50	14.2	16.5	16.7	17.0	18.3	16.9	16.3
60	17.4	18.8	18.3	20.0	21.9	19.6	18.9
70	19.7	20.9	20.8	23.1	25.0	22.3	20.9
80	21.3	23.1	22.9	26.0	28.4	25.0	23.3
90	23.2	25.1	25.6	29.0	31.5	27.6	25.0
100	25.5	27.1	28.2	32.0	34.3	30.1	27.0
110	29.2	29.1	30.5	34.8	36.6	43.5	30.0
120	30.1	30.9	32.1	37.5	38.6	35.2	32.7
130	33.2	32.8	33.6	39.9	39.9	37.4	35.0
140	34.3	34.4	35.4	42.1	20.5	40.2	39.2
			Leachate pH 5.4 (not adjusted)†				
1	0.3	0.5	0	0.3	0	0.1	0
2	0.6	1.0	0	0.5	0	0.3	0
3	0.8	1.2	0	0.8	0.1	0.4	0.2
4	0.9	1.3	0	0.9	0.2	0.5	0.5
6	1.1	0.6	0.4	1.2	0.3	0.6	0.8
8	1.3	1.8	0.7	1.5	0.5	0.8	0.9
10	1.5	2.0	0.9	1.7	0.6	1.0	1.0
12	1.6	2.2	1.0	1.8	0.8	1.0	1.2
14	1.7	2.3	1.2	1.9	0.9	1.1	1.6
16	1.8	2.4	1.3	2.0	1.0	1.2	1.8
18	1.9	2.5	1.4	2.1	1.0	1.3	1.9
20	2.0	2.6	1.5	2.2	1.1	1.4	2.0
50	3.2	3.1	2.5	2.8	2.2	3.1	3.4

* pH was adjusted with acetic acid to aid in evaluating leachate pH effects on limestone utilization or loss.
† Original leachate, pH = 5.4.

TABLE 25. LIMESTONE LAYERED AT FOUR THICKNESSES OVER SAND OR SOIL SOLUBILIZED BY MSW LEACHATES I, II, AND III AFTER 20 PORE VOLUME DISPLACEMENTS

Columns of Soil or Quartz Sand	Leachate Source*	Leachate pH	Metal Enrichment (ppm)	Limestone Thickness (cm)	Limestone Utilized (%)
Davidson c Sand	Leachate I	6.4	Cd - 100	2	1.22
				2	1.41
Davidson c Sand	Leachate I	6.4	Cd - 100	5	0.32
				5	0.36
Davidson c Sand	Leachate II	5.2	Cd - 98	2	2.56
				2	2.71
Davidson c Sand	Leachate II	5.2	Cd - 98	5	1.28
				5	1.32
Davidson c Sand	Leachate III	4.5	Cd - 102	2	6.80
				2	6.40
Davidson c Sand	Leachate III	4.5	Cd - 102	5	2.60
				5	2.90
Ava si c l Sand	Leachate I	6.4	Cd - 97	2	1.51
				2	1.72
Ava si c l Sand	Leachate I	6.4	Cd - 97	5	0.45
				5	0.55
Ava si c l Sand	Leachate II	5.2	Cd - 101	2	2.15
				2	2.23
Ava si c l Sand	Leachate II	5.2	Cd - 101	5	0.32
				5	0.30
Ava si c l Sand	Leachate III	4.4	Cd - 105	2	7.56
				2	7.90
Ava si c l Sand	Leachate III	4.4	Cd - 105	5	2.50
				5	2.20
Kalkaskas s Sand	Leachate II	5.4	No enrichment	2	1.12
				2	1.92
Kalkaskas s Sand	Leachate II	5.4	No enrichment	5	0.38
				5	0.45
Kalkaskas s Sand	Leachate II	5.4	No enrichment	10	0.17
				10	0.15
Kalkaskas s	Leachate II	5.4	No enrichment	15	0.10

* Leachate III is a very young solution (0.5 yr.); Leachate I is the oldest (5 yr.).

limestone.

NATURAL SOIL LINERS AND SALT MODIFICATION LINERS

Natural soil material containing clay (< 2μ particles), even in modest quantities as little as 20%, can be used effectively as liners to either partially or completely prevent downward flow of leachates and other aqueous solutions containing hazardous pollutants. In a series of soil columns packed to densities much greater than natural circumstances, solution flow could be easily controlled at any desired flux. The necessary conditions for complete sealing involves (a) soil material of sufficient clay content (usually 20% or more), (b) uniform distribution of particles of all sizes throughout the soil liner, (homogeneous texture), (c) depth of not less than 45 cm as minimum, and (d) compaction of over 90% maximum density (Fuller et al., 1976 and Fuller, 1980c).

Disposal sites must be surveyed by taking soil cores to the necessary soil depths and logged at 1-ft. intervals. Mechanical analysis of the soil samples will reveal the position, depth, and thickness of the most desirable clay material. The proposed liner material can then be mapped. During excavation of the landfill site, the soil lining material can be removed, then stockpiled separately for lining purposes. If suitable clay soil does not occur in the excavation, it must be brought in from another area.

Addition of a sodium (Na) salt (NaCl or Na_2CO_3) for Na to satisfy more than 15% of the cation exchange complex (CEC), (Decker, 1963; Reginato, 1973) is suggested when complete sealing is desired for salt modified liners. Thorough mixing and application of salt (NaCl or Na_2CO_3) is made just before laying down the liner and compacting is done with usual road equipment.

SPECIALITY LINERS

Hydrous-Oxides of Iron

Evidence is rapidly accumulating in the literature in support of our earlier contention (Fuller et al., 1976b; Fuller 1977a) that the hydrous oxides of Fe, Al and Mn (particularly Fe) of soils play a prominent role in metal attenuation as well as other key chemical and physical reactions. One of the three most important soil characteristics to be highly correlated with heavy metal attenuation was found to be "free" iron oxide (Korte et al., 1976).

When ferrous sulfate (a waste product of mine industry) is applied to soils, it changes rapidly to the hydrous oxides of iron. These iron oxides coat the soil particles forming thin layers which have a potential as active surfaces for attenuation of metallic ions. Preliminary research using the soil column technique, provide evidence of the effectiveness of ferrous sulfate and common iron rust as deterrents to the migration of MSW leachate metals through soils.

Quartz sand and soil columns were prepared by sprinkling the corresponding materials with ferrous sulfate mine waste at a calculated rate of 1%

Fe_2O_3 by weight of the upper 2 cm in the column. The effect of hydrous oxides of Fe on attenuation of Cr and Ni in Wagram s (pH 4.2) and Anthony s l (pH 6.8) are compared in Figure 18. Chromium and Ni migration is clearly retarded by the presence of the hydrous oxides of Fe.

Iron rust scraped from a steel boiler was ground to pass 60 mesh screen and used as a 1 cm barrier over soils to evaluate its influence on retention of CrVI and Ni contained in MSW Leachate I. Data in Table 26 indicates this form of iron oxides possess properties that aid in retention of Cr and Ni through the soils Anthony s l and Wagram s. Metal migration was slowed as much as 26 pvd for Cr and 17 pvd for Ni in Anthony. Similar results were found with Wagram s.

When the soil columns were segmented at 2 cm depth intervals, after breakthrough, and extracted with 0.1 N HCl, the Cr and Ni were found to be concentrated 3 to 4-fold greater at the iron oxide barrier as compared with soil alone segments.

Another point of interest is the highly significant correlation found between iron oxide and total soil Mn. The importance of Mn or hydrous oxides of Mn is not fully known although it is suggested to be less significant in attenuation than iron oxides. The practical research reported here agrees with the pure-system chemical research of Jenne (1968) and Gadde and Laitinen (1974). Data generated from our research (Korte et al., 1975, 1976a; and Marion et al., 1976) show a close and significant correlation between metal attenuation and the abundance of the hydrous oxides of Fe, Mn, and Al.

Nutshells and Similar Organics

The use of pecan nut hulls of various size distribution from 2 mm to 0.1 mm as a barrier over soils failed to improve retention of heavy metals significantly to recommend their use. The added effort and cast of their special treatment for placement does not warrant their use. At most migration of Cd, Ni, and Zn, for example, was delayed only two or three pvd by breakthrough. Moreover, there was serious sealing of the soil to the extent of preventing leachate flow due to the presence of nut hulls. Straw was found to block solution flow even to the extent of closing it off completely. Batch studies with ground pecan hulls, however, indicated that Cd, Ni, and Zn were readily adsorbed similar to the effect of lignin for water purification. Because of the lack of effectiveness of the various organics to functionally remove the heavy metals from MSW landfill leachates when associated with soils in the columns, data are not presented. It should be pointed out, in conclusion, however, that there is positive evidence in the soil column research that over prolonged (20 pvd) contact between the leachates and organic constituents such as pecan hulls, we have positive evidence of accelerated H_2S hydrogen sulfide formation. Under the prevailing anaerobic conditions and high organic residue content, highly reducing conditions were created with the resulting hydrogen sulfide formation and an accompanying precipitation of metals such as Cd, Ni, and Zn. Migration was reduced to almost nothing under these conditions.

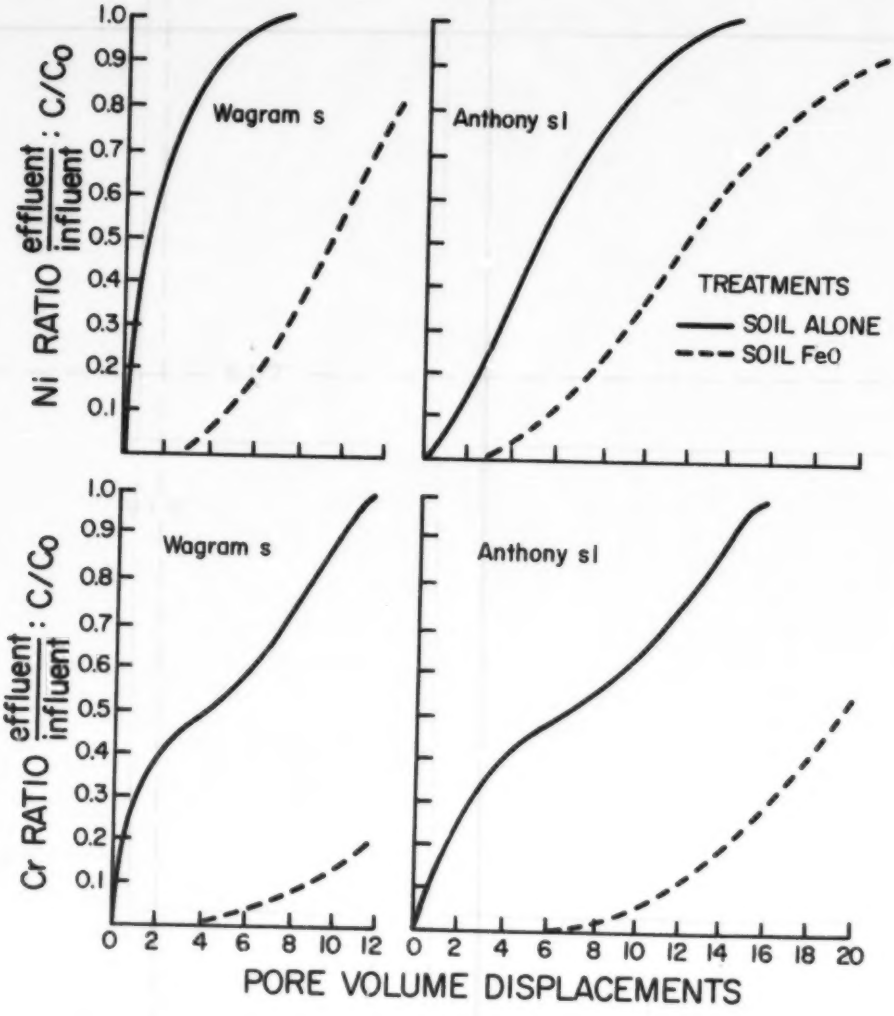

Figure 18. Effect of the hydrous oxides of iron precipitated on Anthony sl and Wagram s on attenuation of CrVI and attenuation of CrVI and Ni of MSW Leachate I.

TABLE 26. EFFECT OF GROUND IRON RUST BARRIER ON ATTENUATION OF CrVI AND Ni IN MSW LEACHATE I PASSED THROUGH ANTHONY sl AND WAGRAM s

	Cr or Ni Appearing in Soil Column Effluent (ppm)*							
	Anthony s l				Wagram s			
pvd	Soil alone		Soil plus Iron Oxides		Soil alone		Soil plus Iron Oxides	
No.	Cr	Ni	Cr	Ni	Cr	Ni	Cr	Ni
3	0.9	0.8	0	0	10	4	2	0.3
6	36	10	0.4	1	59	35	9	11
9	47	32	20	15	75	60	25	39
12	65	49	32	32	98	87	32	45
15	75	60	69	50	--	101	41	76
18	98	79	82	63	--	--	68	100
21	--	95	95	75	--	--	82	98
24	--	100	96	90	--	--	88	101

* Metal content of Leachate I influent was 100 ppm for both Ni and CrVI.

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